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# Handbook of biofuels production

Processes and technologies

Edited by Rafael Luque, Juan Campelo and James Clark



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Human activity requires considerable amounts of energy distributed more or less evenly between three types of activity: industrial, residential and transportation. This is a typical 20<sup>th</sup> century development that resulted from the growth of road transportation. Until the end of the 19<sup>th</sup> century land transportation was based essentially on the use of horses and represented less than 10% of all energy consumption. Biomass in the form of hay for feeding horses has been the main 'fuel' sustaining transportation.

The development of internal combustion engines by Diesel and Otto, approximately 100 years ago was based on the use of biofuels, but with discovery of abundant petroleum reserves there was a dramatic shift in fuels. Transportation now accounts for more than 30% of all energy used in the world and consumes around 83 million barrels of oil per day.

The 20<sup>th</sup> century saw an explosion in the use of automobiles for personal use and trucks for the transportation of goods. There are already more than 600 million automobiles in the world and the number is increasing steadily since the use of the automobile is not only very convenient, but it is also intimately associated with our cultural values. In the United States there are almost 800 automobiles per 1000 people; in China and India this number is 10 times less but quantities are increasing rapidly.

Unfortunately this is a situation that cannot last for very long because the fuels used for present modes of transportation are almost exclusively from petroleum, of which remaining reserves are being depleted rapidly. In addition to that, such fuels are the main source of environmental problems ranging from bad air quality in large cities to regional pollution and the increase of the concentration of greenhouse gases in the atmosphere.

It is therefore urgent to find fuels that could replace petroleum products or develop other methods of propulsion if one wishes to preserve individual transportation.

Of the several technologies in development for that purpose only electrical motors and biofuels seem to be promising solutions. Electrical motors using batteries, where the energy is stored or produced by fuel cells, are making limited progress and in any case will require large additional amounts of electricity to be produced mainly from fossil fuels which are not renewable. One tends to forget that an automobile usually requires 30 kilowatts of power which mean 18 billion kilowatts for an entire fleet. For comparison the total installed capacity for electricity generation in the world is around 4 billion kilowatts.

Biofuels are therefore the more promising option: they are renewable, contribute little to the production of greenhouse gases and do not have the impurities that petroleum derived fuels have. Biofuels already represent a small percentage of the transportation fuels in the world. The 'automobile age', which started with biofuels, seems to be returning to its origins.

The *Handbook of biofuels production* provides a comprehensive discussion of all the aspects of the problem ranging from the feedstocks and production chain to chemical and biochemical production as well as the thermal and thermo-chemical conversion process. Sustainability assessment and policies surrounding the issue are also discussed.

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# Introduction: an overview of biofuels and production technologies

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#### 1.1 Introduction

The urgency to identify a more sustainable way forward for society has become clear with alarming trends in global energy demand, the finite nature of fossil fuel reserves, the need to dramatically curb emissions of greenhouse gases (GHG) to mitigate the devastating consequences of climate change, the damaging volatility of oil prices (in particular for the transport sector) and the geopolitical instability in supplier regions. Currently, energy and the environment are two key hot topics present in all European challenges for the future. With oil prices fluctuating month after month, a cost-competitive and stable solution is needed, especially with an expected 60% increase in the demand of energy for transport by 2030 (the sector expanding in the USA and Europe and specially developing in the newly industrialised and emerging economies of China and India).<sup>1</sup> Transport has also shown the highest rates of growth in GHG emissions in any sector over the last ten years (20% global  $CO_2$  emissions, 25% UK emissions), with a predicted 80% increase in energy use and carbon emissions by 2030.<sup>2</sup>

In order to avoid this dependence on oil and to meet the sustainability goals with regard to GHG emissions originally proposed in the 1997 Kyoto Protocol (confirmed by the European Union (EU) in 2002), clean, secure and affordable supplies of transportation fuels that involve low-carbon technologies are essential.<sup>3</sup>

In this regard, biofuels can make a significant contribution in the short-to-medium term,<sup>4</sup> contributing to energy independence, mitigation of climate change and rural development, being reported as one of the most promising solutions (but not the only one) to help meet targets on the use of renewables and reduced emissions.<sup>5</sup> However, thoughtful analyses of some first-generation biofuels (conventionally produced from 'food' crops, including wheat, maize, corn, sugar cane, rapeseed, sunflower seeds and palm oil) have been recently showing that such alternatives may be little better than traditional fossil fuels, at least, in terms of overall carbon footprint and environmental damage, despite some very promising figures reported in terms of CO<sub>2</sub> emission savings from sugar cane bioethanol use in Brazil.<sup>6</sup>

In contrast, preliminary figures on second-generation biofuels (defined as those produced from non-food sources and including dedicated energy crops such as perennial grasses, short-rotation coppice willow and other lignocellulosic plants as well as waste biomass from agricultural, forestry, municipal solid waste, etc.) in terms of GHG emissions savings, carbon footprint and environmental damage (e.g. deforestation, biodiversity threat, food vs. fuel, etc.) are showing that these can significantly improve on first-generation biofuels. Nevertheless, most technologies for the production of second-generation biofuels from biomass/ waste are still in their infancy and those under development require pre-treatment of the feedstock in many ways (to reduce acidity, floating solids, etc.). So they are far away from being optimised, requiring more research efforts in the future.

In this book, we aim to provide an overview of the different processes and technologies available and those under development for the production of biofuels, with special emphasis on second-generation biofuels produced from biomass. The various biofuels currently produced and/or under development can be grouped according to the processes and technologies employed for their preparation. These include *chemical*, *biological* and *thermo-chemical* conversion.<sup>7</sup>

In the first introductory chapters, details on policies, and socio-economic and environmental implications of the implementation of biofuels (Chapter 2) as well as on life cycle analysis (LCA) (Chapter 3) and the different biofuel feedstocks (Chapter 4) will be presented. The rest of the book is aimed to give a balanced overview on key technologies and processes for the production of biofuels, from first to later generation, as outlined in the next few sections.

#### 1.2 Development of (bio)chemical conversion technologies

Chemical conversion involves a number of widely known and extensively employed processes since the nineteenth century. In fact, the chemical process currently in use for the preparation of biodiesel from biomass (transesterification of oils) is the same as has been used for many years. Feedstocks utilised for the preparation of biofuels are also very similar, with peanut, hemp, corn oil and animal tallow been partially replaced by soybean, rapeseed, recycled oil, forest wastes, trees and sugar cane.

First-generation biodiesel is currently the most common example of a biofuel prepared by chemical conversion. It is currently the most widely developed biofuel in Europe. In 2007, 19 biodiesel plants in the new EU member states were starting operations or were under construction/planning. Relatively large plants (with capacities of 100 000 tonnes/year) can be found in Lithuania, Poland and Romania.

The conventional methodology for the production of biodiesel involves the transesterification of triglycerides (TG) from vegetable oils (palm, corn, soybean, rapeseed, sunflower, etc.) with short-chain alcohols, including methanol and ethanol, to yield fatty acid (m)ethyl esters (FAM/EE) and glycerol as by-products (Scheme 1.1).

However, non-edible feedstocks, including *Jatropha*, *Brasicca* species and microalgae oil, are becoming increasingly important nowadays for the production of biodiesel and are considered to be an important asset for future biodiesel production. The methods of biodiesel preparation can be classified into three



Scheme 1.1 Mechanism of the transesterification process to produce biodiesel.

types: chemical catalytic (base or acid catalysis: homogeneous and/or heterogeneous), biocatalytic (enzyme catalysis: homogeneous and/or heterogeneous) and noncatalytic processes. Several reviews on the preparation of biodiesel from different feedstocks utilising various technologies can be found in the literature.<sup>8–12</sup>

The production of related biofuels via chemical processes (i.e. (trans)esterifications) has also been reported. These biofuels have been specifically developed in research institutions, and commercial processes for their implementation as transport fuels are still under development (see Chapter 7 for more details). For more specific details, the readers are referred to Part II of the book (Chapters 5 and 6 as well as some related content in Chapter 22), in which more detailed information about processes, technologies and biofuels produced will be given.

#### 1.3 Development of biological conversion technologies

Biological conversion technologies for the production of biofuels cover a range of fermentative and biological processes. These basic technologies have also been employed for decades in the production of ethanol (e.g. wine) from sugars via a two-step process of saccharification (hydrolysis of sugars)/fermentation using yeast (Scheme 1.2), followed by distillation of the alcohol produced to obtain a higher degree of alcohol purity.



*Scheme 1.2* Production of bioethanol via fermentation of hydrolysed sugars from energy crops.

Bioethanol is therefore the most common biofuel prepared by biological conversion.<sup>13</sup> It is the most employed biofuel on a world level, with the USA currently being the world's largest producer and Brazil the largest exporter, accounting together for 70% of the world's production and 90% of ethanol used as fuel.<sup>13</sup>

The common feedstocks employed for the production of bioethanol are energy food crops, including sugar cane, corn, wheat, maize and sugar beet, although research on lignocellulosics and woody biomass is under way and these feedstocks have a great potential for future biofuel production.

Through various steps, a wide variety of biofuels can be obtained, including bioethanol, biobutanol and other bioalcohols, biogas and biohydrogen. Biological conversion processes and technologies will be fully addressed in Part III of the book (Chapters 9–11), so we refer the readers to these chapters for further reading on biological conversion processes.

#### 1.4 Development of thermochemical conversion technologies

Thermochemical conversion processes remained largely unexplored until relatively recent despite their important involvement in catalysis.<sup>14,15</sup> Catalytic cracking and/or pyrolysis of vegetable oils and biomass were, until very recently, the most common thermochemical processes for the production of fuels and high-added-value chemicals. Lately, other key thermochemical processes have joined these promising technologies, in particular for the production of biofuels. These mostly include a variety of technologies such as biomass gasification to bio-syngas and other biofuels via hydrothermal upgrading (HTU), reforming and/or synthetic pathways (Fischer–Tropsch synthesis [FTS]), production of bioalcohols from biomass gasification, and so on.<sup>7</sup>

Several feedstocks can be employed in these processes, from virgin vegetable oils (e.g. palm, canola, soybean, etc.) for catalytic cracking to waste oils and fats as well as all different types of biomass, including residual oils, sewage sludge, organic and/or agricultural waste, black liquor and many others.<sup>7</sup> The use of the feedstock is highly dependent on the process and the biofuel to be obtained (e.g. steam reforming and HTU biofuels can be prepared from either dry or wet biomass, irrespectively).

Thermochemical conversion processes and technologies are largely complex and varied. They will be fully described in Part IV of the book (Chapters 12–20), so we refer the readers to these chapters for more information.

#### 1.5 Integration of biofuels into biorefineries

The most promising way to meet the sustainability goals for the future (including the reduction in GHG emissions, reduced dependence on fossil fuels, etc.) is to promote the utilisation of low-carbon technologies to convert biomass into a variety of chemicals, biomaterials and energy, maximising the value of the biomass while minimising waste.

This integrated approach has been defined as 'the biorefinery concept' and has recently received a great deal of attention in many parts of the world.<sup>16,17</sup> The biorefinery of the future will be analogous to today's petrorefineries<sup>18,19</sup> in such a way that many different industrial products will be generated from biomass (Fig. 1.1). These include low-value, high-volume products, such as transportation fuels (e.g. biodiesel, bioethanol, etc.), commodity chemicals and materials, as well as high-value, low-volume products or speciality chemicals, such as cosmetics and nutraceuticals.

Energy and, most precisely, biofuels are the main driver for developments in this area, but other relevant products are expected to be developed as biorefineries become more and more sophisticated with time.

Several types of biorefineries have been described in the literature, mainly phase I, II and III biorefineries, depending on the variety of feedstocks, processes and products obtained in the facilities. Biofuels are part of the products obtained from the treatment of a wide variety of biomass feedstocks, actually playing a major role in the economics of the process. This highly interesting topic will be fully tackled and expanded in the Appendix chapters (Chapters 21 and 22), in which types of integrated biorefineries, processes for biofuels production and by-products and related subjects will be revised.

Last but not least, engine tests are of utmost importance to test the feasibility of biofuels implementation in the future. In this way, Chapter 23 accounts for a nice contribution, combining a revision with experimental results on the implementation of biofuels (both pure and as blends) in engine tests.



*1.1* Comparison of petro- versus biorefinery (from *Introduction to Chemicals from Biomass*, Edited by James Clark and Fabien Deswarte; Copyright John Wiley & Sons, 2008; reproduced with permission).

#### 1.6 Future trends

Lignocellulosics and algae have been recently considered the most promising alternatives for the production of later-generation biofuels. A full account of the production of a wide range of second-generation biofuels from lignocellulosic biomass (e.g. wood, grasses, agricultural and forestry waste) is given in Parts III and IV of this monograph. The process is identical to that described in the production of first-generation bioethanol: decomposition of the material into fermentable sugars (hydrolysis) and transformation of the sugars into bioethanol (fermentation). The main changes are in the processing technologies and the feedstocks that usually account for the majority of the plant cost. Lignocellulosic biomass comprises three main components: cellulose and hemicellulose (complex carbohydrate polymers), accounting roughly for about a 70–75 wt% of the lignocellulose, and lignin (Fig. 1.2).

A mixture of enzymes (cellulases and hemicellases) different from those used in the first-generation bioethanol production are employed in the hydrolysis step. Lignin is obtained as a by-product of the process that can be burned to produce heat and power for the processing plant and potentially for surrounding homes and businesses. It has also a great potential as it is hoped to become a future source of aromatic chemicals and materials. Alternative organisms also need to be employed due to the impossibility of traditional yeast and bacteria to process the pentose (C5) sugars derived from hemicellulose.<sup>20</sup> We refer the readers to



*1.2* Schematic representation of the components of lignocellulosic biomass and their enzymatic degradation.

Chapters 8 and 14–18 for more detailed information on advanced technologies for the processing of lignocellulosic feedstocks.

Algae is the second relevant feedstock with a great potential for future development. It has not been included as such in the monograph, but we believe that Chapters 4 and 8 will give some details about these microorganisms for the production of biofuels.

Microalgae are sunlight-driven cell organisms that convert atmospheric  $CO_2$  (via photosynthesis) into a plethora of chemicals, including methane, hydrogen, polysaccharides and oil.<sup>21–23</sup> Interestingly, the production of algal oil is remarkably more efficient compared with conventional oil crops, providing higher oil yields (up to a 75% dry weight) and lower land area utilisation (Tables 1.1 and 1.2).

The process involves the extraction of the oil from microalgae and subsequent transesterification with alcohols using homogeneous or heterogeneous catalysts (in a similar way to that of biodiesel obtained from (non)edible feedstocks) to give biodiesel.

Despite significant advances in the field, which have been recently reported in the area of biofuels produced from algal oil, there are several drawbacks that

Microalgae	Oil content (% dry wt.)
Botryococcus braunii	25–75
Chlorella sp.	28–32
Cylindrotheca sp.	16–37
Nannochloropsis	31–68
Nitzschia sp.	45–47
Schizochytrium sp.	50–77

*Table 1.1* Microbial oil content (% dry weight) of various algae species<sup>21,22</sup>

*Table 1.2* Comparison of oil yield versus required land for different biodiesel feedstocks in the USA<sup>21,22</sup>

Crop	Oil yield (L/ha)	Required land (M ha) <sup>a</sup>
Microalgae <sup>b</sup>	136,900	2
Microalgae <sup>c</sup>	58,700	4.5
Oil palm	5,950	45
Jatropha	1,892	140
Canola	1,190	223
Soybean	446	594
Corn	172	1540

<sup>a</sup> To meet 50% of all US current transport consumption.

<sup>b</sup> 70% (w/w) oil yield in biomass.

<sup>c</sup> 30% (w/w) oil yield in biomass.

currently limit its widespread utilisation, primarily the economic feasibility of the technology.<sup>24</sup>

The recovery of such bio-oil from algae is a very challenging task. The algal broth produced in the biomass production generally needs to be further processed to recover the biomass<sup>24,25</sup> and then the concentrated biomass paste is extracted with an organic solvent (e.g. hexane) to recover the algal oil that can be transesterified into biodiesel. Furthermore, the valorisation of the dry residue of the algae is not normally taken into account in current processes, and this largely implies a significant increase in costs as these algal residues need to be disposed of/removed upon extraction.

On the other hand, algal oil is rich in long-chain polyunsaturated acids, including eicosapentaenoic (EPA; 20:5 n-3) and docosahexaenoic acids (DHA; 22:6  $\omega$ -3), which are generally undesirable in conventional biodiesel due to the negative impact of the polyunsaturation on the oxidation stability. The presence of EPA and DHA is not contemplated in the EU (EN 14214 and EN 14213, biodiesel for transport and heating) and US (ASTM D6751) quality biodiesel standards that specify a limit of 130 g (EN 14213) and 120 g (EN 14214) iodine/100 g of biodiesel (iodine value). Storage issues arising from the oxidation instability may be overcome through either chemical transformations (e.g partial catalytic hydrogenations of the polyunsaturated compounds in the oil)<sup>26</sup> or genetic modification of certain species.<sup>7,24</sup> It is yet unclear as to how the presence of much more saturated FAM/ EE will affect the cold performance (CFPP) of the biodiesel.

These main drawbacks remarkably influence the economics of the process, in which problems related to capital infrastructure costs, contamination through openpond systems and costs associated with harvesting and drying of the algae may also have a major contribution. A full and precise estimation of the economics of the process is therefore needed in order to demonstrate its feasibility,<sup>23–25</sup> in which the valorisation of the algal residue (potentially via gasification to syngas and/or other biofuels) is believed to be critical to improve the economics of the process.

The potential for biofuels has been recognised throughout the twentieth century, but the new century has brought with it a widespread realisation that the petroleum age is coming to an end. The use of petrol fuel replacements has generated a lot of controversy; ideally, they should contribute to global sustainability, ensuring the energy supply and meeting the GHG targets (as well as being profitable and costcompetitive as much as possible) without compromising the economies, culture, societies and the environment of our future.

There are in our views exaggerated expectations from second-generation technologies which probably will take a long time to materialise, with topics such as fuel 'versus' food and the consequence of land use changes on GHG emissions being 'politicised'.

These important issues should however not let us get distracted from the potential benefits of biofuels and, more widely, of biomass exploitation. It should rather encourage us to redouble our efforts to research low-carbon technologies

for the production of later-generation biofuels (and biochemicals) from low-value waste biomass, with properly measured and reported environmental impacts. A combined effort from politicians, economists, environmentalists and scientists is needed now, more than ever, to address the issues of the progressive incorporation of biofuels in our society and to come up with alternatives, policies and choices to advance the key technologies for a more sustainable future.

#### 1.7 Acknowledgements

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2

# Multiple objectives policy for biofuels production: environmental, socio-economic and regulatory issues

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**Abstract:** This chapter illustrates and discusses main objectives of biofuels policies viewed under multidirectional effects on economy, energy and environment. The analysis touches multiple effects of biofuels production and use such as the need for guaranteeing energy security and supply, environmental protection and land-use change, the expansion of rural areas and food safety and the increasing institutional support for biofuels policies including the contribution of these to climate change mitigation.

**Key words:** biofuels, feedstock, land use, rural development, climate change mitigation.

#### 2.1 Introduction

Since their introduction in the supply chain, biofuels contributed to the reduction of carbon emissions. It is this evidence, together with advances in technological progress for renewables use and recent development of international agreements on climate change, that suggests to governments the adoption of new practices to enhance the agricultural sector. A renovated agricultural system was launched for biofuels feedstock production. This, in turn, served as a stimulus for countries facing current unbalances of imported energy commodities to search for new energy supply and security initiatives. Additionally, current biofuels feedstock production and future bioenergy and biorefinery practices are instrumental in the enhancement of rural development and the creation of further policy tools in the biofuels industry as well as the agricultural sector. However, this scenario is not without drawbacks. The positive and negative synergies occurring across a multitude of biofuels objectives should be carefully addressed. The aim of this chapter is to illustrate and discuss main objectives of biofuels policies viewed under multidirectional effects on economy, energy and environment. The chapter is organised as follows: Section 2.2 illustrates biofuels and bioenergy seen as energy security and supply; Section 2.3 discusses environmental and land-use concerns linked to biofuels practices; Section 2.4 emphasises the risk for food safety and the need for the development of marginal areas when considering biofuels activities; Section 2.5 describes current biofuels policy support and delineates future scenarios for climate change mitigation; finally, Section 2.6 concludes.

#### 2.2 Energy security and supply

In developed and developing countries facing fluctuations of oil prices, the improvement of energy security and supply is increasingly becoming a fundamental reason for implementing biofuels policies. Rich and industrialised countries driving their economies on fossil fuels and oil products and derivates are experiencing shortage of finite resources with a consequent high risk of depletion and exhaustion. In addition, intensification of trade in oil commodities creates trade unbalances for those countries which are strongly dependent on imported energy commodities such as the European Union, United States, China, Japan and India.

In a number of countries, regulation is currently being adopted or under scrutiny to favour energy supply and safety. The following description will focus on the European Union, United States and Brazil. In the European Union, a new set of energy regulations are changing current and future scenarios of energy use and supply. The Commission Directive 2009/28/EC on the 'promotion of the use of energy from renewable sources' which abolishes the previous Biofuels Directive (Commission Directive, 2003/30/EC) and the Commission Directive 2001/77/EC on electricity from renewables. The new legislation body put in place an exclusive framework for renewable energy production within Member States. In particular, the Directive 2009/28/EC sets reference values of energy from renewables computed from estimates of gross final demand by 2020.

These reference values correspond to the achievement of the European Union '20–20–20' strategy which is a fundamental voluntary policy adopted in March 2007 by the European Commission to further attain the goals of the Kyoto Protocol. The 20–20–20 policy establishes by 2020 to reach a target of 20% reduction of greenhouse gases (GHGs) by using 20% renewables. Given this ambitious scenario, Member States are required to set their shares of energy from renewables and create measures to promote the development of a competitive energy market ensuring access to electricity network from renewables. The Directive also promotes biodiversity protection of threaten species in those lands where biodiesel and bio-liquids production would have negative impacts on flora and fauna. Raw materials used in biodiesel and bio-liquids production should therefore achieve the status of 'sustainable', by competent bodies, before being processed.

In the longer term, the 2007 Renewable Energy Road Map (European Commission, 2007) specifies the adoption of a minimum ten per cent consumption of biofuels in the transport sector. Biofuels use in the transport sector would contribute to 14% of total market fuels (corresponding to about 43 million tonnes of equivalent oil) and the share may increase from either current bio-ethanol production in Sweden or biodiesel production in Germany and other European Union countries or other feedstock such as ethanol from straw, rapeseed oil, palm oil and second-generation biofuels mainly obtained from wood processes (De Lucia, 2010).
Over the last decades, Brazil has become one of the major biofuels producers. Although regulation on biodiesel entered into force in 2004, Brazilian production of biofuels is mainly centred on ethanol from sugar cane. Contrarily to biodiesel, ethanol is being processed since 1975 which makes Brazil the second-largest producer of transport fuels over a 30-year period. The abundance of land and proper climate conditions for sugar cane production and the possibility of transport subsidies ensuring full ethanol distribution within the country are important factors for the evolution of such industry. Several reasons have been adopted in favour of governmental support for biofuels in Brazil. These vary from purely economic-profit oriented ones to those including environmental concerns, energy security and rural development. Energy safety nonetheless was encouraged since the oil crisis during the 1970s when Brazil had to overcome national debt crisis by borrowing foreign capital. Ethanol production was then seen as a safe way to reduce import and interest costs. Simultaneously to the expansion of the ethanol industry, major employment creation occurred in the biofuels sector favouring the expansion of unskilled workers in rural areas and the formation of more than 60 000 small-sized farmers countrywide (Moreira, 2006).

The success of the Brazilian experience also lies behind a direct or indirect connection with several synergies such as those with other economic sectors. In this case, established relationships with the sugar and electricity and heat production markets are relevant. The sugar market played a primary role in driving the ethanol growth within and outside the country. On the supply side, the degree of price elasticity between sugar and ethanol (e.g. 0.20, Elobeid and Tokgoz, 2008) and the international volatility of sugar prices pushed Brazilian farmers toward ethanol production. Productivity of the ethanol sector also rose substantially to more than 100% (Moreira, 2006) during the 25 years period from 1975 to 2000. The electricity and heat production industry were also fundamental to boosting biofuels production as these served both the internal and foreign markets with using by-products from sugar cane. By the end of 2010, the amount of electricity from biomass mainly obtained from sugar mills is expected to be around 7.8 GW (Empresa de Pesquisa Energética, 2008). The Brazilian government played nonetheless an essential role for the enhancement of the biofuels industry. In particular, it provided incentivising measures (see also Section 2.5) throughout the entire biofuels chain production (including support to technological advances in the sector) and to final end-users. Most of all, the establishment of a transparent institutional framework has guaranteed full competitiveness within markets. However, it was not until recent years, where consumer habits for fuel-switching engine cars increased rapidly, that ethanol production took off considerably. In 2006, 75% of new car models were produced with fuel-switch technology engine. New sugar mills implementations are expected to be operative by 2010 (Empresa de Pesquisa Energética, 2008) and generate diversified energy and food output: from electricity grids, to biodiesel plants, to rotation plantations for food crops.

Under Obama's presidency, the United States (joint world leader of biofuels production with Brazil) is currently experiencing a revision of its Renewable Fuel Standard (RFS) policy (Environmental Protection Agency, 2010) adopted under the Energy Policy Act (EPA) in 2005. Recent economic recession and other factors (i.e. the existing mismatch between biofuels distribution requirements and current infrastructures for petroleum industry) are preventing the United States reaching its congressional goals of the Energy Independence and Security Act (U.S. Senate, 2007). This requires 100 million gallon biofuels from biomass by 2010 and 36 billion gallon per year by 2022. Sustainability of supply chain is being threatened by high transaction costs in meeting the requirements between feedstock production and research and rural wealth. Likewise, although the accomplishment of expected results from currently funded projects, lack of integration at all levels of government is also causing delays achieving national biofuels targets (Environmental Protection Agency, 2010). The existence of a 15 billion gallon cap on ethanol biofuels from cellulosic by 2022 is posing further challenges to EPA's current policies for distribution, transportation and storage of current and future ethanol production. The need for a new strategy is desirable. The new 2010 and beyond EPA programme on renewable fuels released on 10 February 2010 by the President's Biofuels Interagency Working Group (2010) intends to adopt a strategic approach to optimise and integrate biofuels production development at all levels. This would mean not only to ensure coordinated measures for research, demonstration and commercialisation phases, but also guarantee coherence and efficiency of management across government funding, farmers and companies.

To ensure management efficacy in the biofuels industry, the creation of a small management team was proposed to help establish deliverables and corrective measures to keep projects on track, monitoring results throughout the entire biofuels supply chain and report progress works to the Biofuels Interagency Working Group. The reinforcement of the biofuels supply chain management is also established by the involvement of federal departments such as the Office of Science for research issues; the Feedstock Development and Production units at the USDA addressing environmental, economic and education concerns for biofuels chain; Department of Energy Efficiency and Renewable Energy to assist the setting up and development of pilot projects; and other departments at EPA and USDA for monitoring and regulatory procedures, sustainability issues, policy support and technical assistance. It is vital for integrating various efforts put in place from this multitude of agencies and departments and also for the success of deliverables and targets to ensure a continuum in the biofuels chain management. EPA's strategy is also pursuing first- and second-generation biofuels development together with boosting third-generation biofuels advances through financial support actions, feasibility studies, technological improvements and new markets for corn-based ethanol production. Finally, a fundamental aspect of the EPA's biofuels management is an integrated approach to economic, environmental and social concerns.

## 2.3 Emission reductions, land use and other environmental impacts

There is a wave of debate whether biofuels production and use effectively reduces carbon emissions. Undoubtedly, the universal answer does not exist yet. To assess environmental effects of GHG reductions one should consider the combined net effects of the energy technology associated with biofuels, carbon emissions, land conversion and agricultural production. These lead in fact to two types of effects: GHG reduction from land conversion for biofuels feedstock production (direct impact) and GHG reduction from off-site land conversion for biofuels feedstock production (indirect impact).

Accounting for these effects creates the opportunity to measure direct and indirect emission reductions. It is important for policy makers to obtain, as precisely as possible, a picture of the regulation's potential on biofuels production. It is crucial for example, given that the majority of policy support is in the form of a subsidy, to understand all net effects from biofuels feedstock production (and consequent biofuels use) on GHGs to efficiently assess the subsidy rate. Current debate mainly focuses on the quantification of indirect effects. These results are difficult to quantify because an increased dependence on biofuels would mean increased demand for land to meet the requirements of off-site land conversion. As a consequence, significant zero (or negative) net impacts on climate change (i.e. in terms of increasing GHG emissions) would result. The risk of considerable carbon emission coupled with land use has been, until present, mostly ignored. Few studies (Hill et al., 2006; Zah et al., 2007; Searchinger et al., 2008) assessed the magnitude of increasing emissions from land-use changes, and there is still concern on the quantification issue for indirect effects. Substantial efforts are therefore needed to address the correct measurement of indirect effects on GHGs from land-use changes for biofuels feedstock production.

The conversion of land for agricultural activities (i.e. from forests to agricultural lands) causes considerable carbon emissions through time because this is released at consecutive stages during the conversion process. Positive net carbon costs would be obtained with the benefits arising from displacement effects of fossil fuels emissions gained over new land use for biofuels production. However, since time plays an important part when computing net benefits, it becomes essential for policy makers to consider a 'justified' period of time consisting of the lifetime of indirect effects of land-use changes. Some studies (Righelato and Spracklen, 2007) consider a 30-year time a justified period for indirect effects to occur. This is though based on the average time frame of ethanol plants and, as a consequence, the land change occurs as long as 30 years when ethanol feedstock production most probably takes place. Other studies (Renewable Fuels Agency, 2008) consider the payback period (the time that land conversion needs to give positive GHG impacts) of biofuels production arguing that most of carbon effects are intensified during the first ten years of land conversion because the release of

carbon is more sensitive. Marshall (2009) argues on two time periods for the lifetime of biofuels feedstock production: The first is a 'project horizon', the effective time period needed for biofuels feedstock to grow on a specific (converted) land. In essence, the time for which the converted land is planned to be used for feedstock production. This period could also be shortened or amplified according to changes occurring in biofuels technologies or at policy level (i.e. changes in the subsidy rate). The second is 'impact horizon' which considers the environmental aspect (carbon emissions) over the converted land for biofuels feedstock production. This would undoubtedly be not necessarily as long as the project horizon time span because its effects are generally prolonged over time. While, in fact, GHG reductions linked to biofuels production terminate as soon as the biofuels production (on that land) ceases, the consequent emission reductions would still remain in place (Marshall, 2009). Therefore, the distinction between these two time effects is important to assess effective policies for adequate land use. Knowing about the time periods for project and impact horizons would also mean recognising economically viable biofuels land-use changes and, consequently, efficient carbon emission strategies.

A similar issue to consider for measuring net indirect effects of land conversion is an 'efficient' discount rate for comparing the outcomes of various projects for land-use changes into biofuels activities. Some (Howarth, 2005) argue against high discount rates which reflect time uncertainty for future outcomes in investments for biofuels activities. Others (Marshall, 2009) assert that discounting functions should also be seen under a physical carbon content perspective. The aim is that comparisons across investments activities for setting up biofuels production should also be performed so that environmental considerations for payback mechanisms are consistent with sustainable practices.

Other environmental impacts of biofuels production can be found in numerous life-cycle assessments, mainly for biodiesel, in the transport sector (Booth *et al.*, 2005; Bozbas, 2008). These studies normally conclude with recognising the positive effects in terms of GHG emission reductions. As concerning other pollutants, biodiesel and ethanol production also produce zero emissions in terms of sulphur dioxide (which, in general, is emitted during the burning of fossil fuels). Relevant reductions can also be seen in carbon monoxide and hydrocarbons (Nwafor, 2004; Schmidt, 2004). The literature seems controversial about the nitrogen oxide and dioxide emissions. Nitrogen oxide emissions in vehicles using a biodiesel engine are found at slightly higher levels than those in a conventional diesel engine. However, a modification of the engine would reduce these levels, and therefore this negative effect could be considered of no relevance (Booth *et al.*, 2005). Nitrogen dioxide emissions would instead occur from biofuels feedstock processes which have potential effects on the ozone layer (Franke and Reinhardt, 1998).

Feedstock processes either for biodiesel or for ethanol production also present three further environmental effects such as fertility of soils, biodiversity and hydrological impacts (Kartha, 2006). Furthermore, large-scale use of monoculture

for biofuels production also has an impact on the environment through the excess use of fertilisers and pesticides. Biofuels feedstock production significantly affects the ecosystem either boosting biodiversity or threatening existing species and the natural habitat. On one hand, the use of set-aside lands for biofuels feedstock production causes, for example, water pollution (because of the use of fertilisers and pesticides) and affects local biodiversity. On the other hand, biofuels production offers a good example of biodiversity protection compared to other conventional agricultural practices. In several countries (e.g. Brazil) existing regulation requires leaving a proportion of land to natural flora and fauna to preserve biodiversity losses (Turley et al., 2002). Biofuels production poses a number of challenges to the management of soil fertility. First, recycling of small organic and plant nutrients is possible. Second, current agricultural practices (in particular in developing countries) for soil management depend on the wasted crop (though this is more relevant for biomass feedstock than biofuels). In addition, feedstock nutrients can be retrieved during land conversion processes and applied to the crop field for biofuels production rather than putting these in landfills. Finally, hydrological effects are also important. Some bioenergy crops require the same amount of water irrigation as food crops (i.e. sugar cane). However, as for food crops, it is essential for bioenergy crops to be guaranteed water infiltration from rainfall to avoid inefficiencies from water wastes.

## 2.4 Food safety and development of rural areas

At the heart of current debate on biofuels markets, the development of rural areas and food safety issues are of great concern. When considering the nexus between biofuels and rural development, four main aspects are specified in current literature: (1) social benefits of biofuels policy; (2) food security versus land management; (3) public sector intervention; and (4) enhancement of secondgeneration biofuels from non-food crops. Dufey (2006) offers a comprehensible review of social benefits of biofuels production accruing in developing as well as developed countries. In general, increase in employment generation in rural areas is mostly dependent on the type of crop used for biofuels production (e.g. sugar cane), although this should be seen according to market structure and income distribution. Given that agricultural production in rural areas is mostly labourintensive, extra demand for agricultural products is likely to increase wages and employment. There are significant effects on job creation by either employing feedstock conversion practices or acquiring feedstock locally. Small-sized farmers could accelerate multiple income effects (Hazell and Pachauri, 2006). As a consequence, increased liquidity in local markets would have positive repercussions on the economy of rural areas. In Brazil or United States, for example, large firms control the bioenergy industry, whereas in developing countries small-sized growers organised in cooperatives represent an important link between large corporations and independent farmers.

The second aspect of biofuels policy is the question of food safety versus land management. Rosengrant et al. (2006), with the use of the IMPACT model (developed by the International Food Policy Research Institute at the Consultative Group on International Agricultural Research), examine the interactions between the demand of land for biofuels feedstock and the demand of land for food purposes and analyse how these interdependences affect food commodities and prices. The authors consider three main scenarios: (a) a massive growth in biofuels and no changes in productivity; (b) use of second-generation biofuels in current agricultural practices; and (c) considerable biofuels growth with changes in agricultural productivity and switch to production of second-generation biofuels. Results suggest in case (a) a remarkable increase in food prices causing sizeable losses in rural areas in developing countries. The need of subsidising biofuels would then arise with consequent distorting mechanisms due to unproductive agriculture and bioenergy sectors. In the second scenario (b), a change in technology would increase food price but at a lower rate compared to the first scenario. Finally, the last scenario (c) shows that a combination of technology improvements and productivity increases would alleviate shocks in food prices and favour the growth of small-sized farmers devoted to the supply and development of local markets.

The International Centre for Trade and Sustainable Development (2008) argues on competition of land for food versus land for biofuels feedstock. In principle, higher food prices would not automatically affect poor people. Rather, increases in food prices could be seen as an income generator for farmers working in poor rural communities. This vision is, however, not totally shared by a number of researchers (Naylor *et al.*, 2007; Goldemberg, 2008) and institutions (World Bank, 2008). In particular, Goldemberg (2008) recalls that the problem of land competition over food and biofuels production should be seen as a problem of food safety versus climate issues. The entire 'food question' is the consequence of a renewed interest in the agricultural sector because of the ease of profits in biofuels energy production. Extended agricultural practices affect increases of indirect emissions of carbon as well as other dangerous GHGs (e.g.  $NO_x$ ) and contribute to deforestation and biodiversity losses.

Naylor *et al.* (2007) argue on the increasing rate, over the last years, in demand for energy commodities as incomes rise. This scenario would determine increases in energy as well as food commodities prices reversing, in the latter case, what was once the long-term declining trend in agricultural prices. The volatility of food prices causes strong impacts on undernourished population which typically spends almost all its income on food commodities. Linkages between food and energy prices are inevitable. While these were once seen in terms of agricultural energy inputs, nowadays these could be determined by the revenue prices of feedstock for biofuels production required to cover production costs. At international level, these relationships would be most difficult to determine given a number of determinants affecting food and energy prices such as the demand elasticity of agricultural commodities, national policies over land management for

biofuels and food crops and the presence of institutional support to incentivise biofuels production. There are only few quantitative models which explain international transmission of price volatility for biofuels and agricultural commodities (Abdulai, 2000; Conforti, 2004; Schmidhuber, 2006; Peri and Baldi, 2008; Hertel and Beckman, 2010), and these focus either on national case studies (i.e. Ghana, Iran, Italy, United States) or selected agricultural crop and biofuels commodities. A further implication on food security and undernourished population is food aid. There is an inverse relationship between shipment aids (from richer countries) and food prices (Falcon, 1991; del Ninno et al., 2007). Countries relying on food aid (i.e. Sub-Saharan African or Southern Asian countries) are subject to substantial domestic critical effects (i.e. production and land availability, internal market prices instability, government responses) in the presence of global food price increases. The general trend in food and energy prices and the consequences on world food safety is also recognised by the World Bank in its recent document submitted for and approved by the G8 meeting in 2008 (World Bank, 2008). The rise in food and energy prices (Fig. 2.1) causes important macroeconomic effects mostly on domestic economies.

Inflation, for example, is hitting developing economies that are fighting to keep the percentage between five and seven per cent (Fig. 2.2). The same countries are now experiencing fluctuations in inflation rates because of price increase in oil, food and other basic commodities.



*2.1* Commodity price indexes in nominal terms (author's elaboration on *World Economic Outlook Database* [International Monetary Fund, 2009]).



*2.2* Inflation rates for selected economies (author's elaboration on *World Economic Outlook Database* [International Monetary Fund, 2009]).

Worsening of balance of payment also causes a reduced capacity of developing countries to sustain (by reducing official reserves) import exposure in the immediate future. Most of the emerging economies show in fact a negative trend in changes of official reserves over the last decade (Table 2.1).

Furthermore, when emerging economies are also energy-intensive importers, a damaging effect in terms of trade contributes to exacerbate their institutional and economic vulnerability. Pressures on wages and other costs become inevitable for

Year	Africa	Central Eastern Europe	Commonwealth of Independent States	Developing Asia	Western hemisphere
1999	-1.169	-9.987	-6.521	-25.994	5.659
2000	-13.321	-4.445	-20.376	-16.578	-6.701
2001	-10.393	-1.719	-14.367	-58.825	1.824
2002	-5.749	-8.049	-15.079	-110.84	1.466
2003	-10.878	-10.761	-32.697	-166.8	-33.611
2004	-31.595	-12.82	-54.896	-258.75	-22.176
2005	-43.233	-44.059	-77.092	-235.16	-33.492
2006	-54.505	-32.668	-127.79	-322.57	-50.298
2007	-61.079	-36.272	-168.05	-629.46	-133.09
2008	-53.553	-5.665	33.187	-437.54	-51.479
2009	13.852	-1.873	20.807	-329.3	-19.322

Table 2.1 Changes in official reserves in billion US dollars

Source: World Economic Outlook Database (International Monetary Fund, 2009).

such countries where fiscal and monetary policies are too vulnerable to food and energy price fluctuations. This and the rise of income inequality (including the aggravation of poverty) in developing countries asks for immediate implementation of adequate policies.

G8 as well as United Nations countries agreed on a number of initiatives. First, a continuous support to fund the World Food Programme in addition to the provision of financial and technical assistance for the supply of agricultural commodities. Second, in a longer term perspective, investments in agricultural and rural infrastructures to guarantee market access especially in African, Southern Asian and small island countries. Third, enhancing technological investments in developing as well as developed countries for second- and third-generation biofuels from cellulose-based ethanol products. And fourthly to promote the reduction in trade tariffs for biofuels commodities and improve the functioning and implementation of international agreements (e.g. the Doha Round) affecting agricultural markets (World Bank, 2008).

The public sector plays a substantial role in the development of rural (and also industrialised) areas and the mitigation of competing food markets when enhancing biofuels activities. The use of land for biofuels feedstock could have negative impacts on the demand for food commodities causing food prices to increase due to scarcity of productive land for food production. Lack of sufficient natural resource endowments for biofuels crops causes consistent losses especially in poor areas. A price increase in food commodities would in fact be detrimental to those farmers experiencing a net deficit of food production. Unjustified repercussions on consumer prices would then occur (in rural/poor areas) where demand elasticity of agricultural products is high. To avoid the occurrence of vast social costs, public intervention becomes a necessary tool which helps reduce market failures and rebalance trade-offs between food and bioenergy through adequate supporting policies (Hazell, 2006). These can be in the form of incentives: to increase the productivity of food production such that additional land and water can be used for biofuels crops; to convert infertile lands to second-generation biofuels; to use by-products from food production to boost bioenergy commodities; and to remove barriers to trade and promulgate the benefits of competitive markets for biofuels commodities at any scale of technology. Supporting policies would also guarantee independent and small-sized farmers in less developed countries the opportunity to process bioenergy commodities at local level. In addition, the identification of all stakeholders in the biofuels chain becomes fundamental when setting policy targets in the food sector at national level. The Brazilian example is a success. First for the recognition of new demand in environmentally friendly automobile industry through the use of ethanol fuels; second for setting subsidies to enhance economies of scale in the agricultural as well as the automobile sector; third for integrating the private sector in the public management for electricity supply from bioenergy products; and fourth for creating new stimulus to rural activities employed in biofuels production.

There exists, undoubtedly, a connection between developed and rural areas for biofuels production. Large-scale biofuels activities in developed countries may reduce the export of food products pushing the prices of these goods up. This would in turn positively affect rural areas in developing countries benefitting from higher net surpluses in food commodities. Contrarily, higher world food prices would also mean scarcity of food products for poor households living in rural areas. When this negative effect is counterbalanced by higher employment and income perspectives in the biofuels industry, the net impact at aggregate social level generates economic growth led by the agricultural system. From this angle, biofuels chain can make a substantial contribution to combat poverty and improve food safety. The production of energy from bioenergy crops, together with the sustainable use of local resources, could result in higher standards of living for the rural society as a whole. Additional energy resources to the local community would finally contribute to the local development of rural economic activities including agricultural enhancements and food security.

A final aspect to discuss concerning the link between biofuels/bioenergy and rural development is the enhancement of second-generation biofuels. Studies on jatropha production in African countries (Venturini Del Greco and Rademakers, 2006) indicate several benefits at community level. These benefits derive from an integrated approach run by public enterprises (and managed by private firms) to jatropha production such as electricity consumption, milling services, additional oil for sale purposes, by-products for use in soap manufacturing and fertilisers use. Van der Plas and Abdel-Hamid (2005) argue in favour of biofuels from wood production in rural areas in Sub-Saharan African countries. Of relevant interest is the demand from urban centres and the transparency of relationships (contractors, distribution of rents, etc.) between these urban centres and rural areas supplying biofuels. The intricate but efficient legal network thus running in these areas contributes either to the enrichment of small farmers' wealth or to the sustainable resource use.

## 2.5 Biofuels support policies

The increasing support for biofuels production over the last years in both developed and developing countries has been taking shape under a variety of policy tools aiming at several objectives: from increasing biomass, to land conversion, redistribution issues, fuel consumption, fuel and food prices, to cite a few. Subsidies, under various facets across countries, are the most commonly used measure in support of biofuels production. With a direct subsidy, for example, governments sustain farmers for every unit of biofuels/biomass produced. In European Union, United States, Brazil and now also in several developing countries (OECD, 2008), direct subsidies promote the use of set-aside lands for non-food crops cultivation and help in reducing various input costs such as fertilisers, feedstock and distribution.

Economic reasons advocate subsidies for biofuels production given that these cause reduction in GHG emissions. Therefore, to recognise biofuels for emission reduction and improving environmental quality, a GHG credit mechanism in the form of a subsidy is being considered as a viable instrument to incorporate (credit) that externality in the final price of biofuels commodities. Evidence of distortionary effects of subsidies is nonetheless common in economics such that caution should be used when implementing such tools (Koplow, 2006; Steenblik, 2007). The distortion would arise when using subsidies for unproductive investments with consequent market inefficiency (i.e. in production, consumption and prices) causing loss of well-being to the society and damaging the natural environment. Further debate considers the relationship between crude oil prices and food prices (Tyner, 2007). Over the last years, the rise in crude oil prices is putting considerable pressure on primary food prices (i.e. corn prices), and having a fixed subsidy on biofuels feedstock (e.g. ethanol) would certainly not help to keep food prices down. Contrarily, subsidising the biofuels industry is pushing higher investments in the sector causing food prices to increase with more damaging repercussions in the economies of the developing world. Tyner (2007) considers alternative policy mechanisms to a fixed per unit subsidy such as a variable rate linked to crude oil prices or higher subsidies to enhance third-generation biofuels (i.e. cellulosebased ethanol) to reduce agricultural prices and re-establish the balance between land for food cultivation and land for biofuels feedstock.

Other measures than subsidies can also be advocated for biofuels production. These are in the form of investment grants (from government and/or public institutions) to ensure that adequate start-up phases for agricultural feedstock conversion and efficient distribution at pumps take place. Furthermore, in the United States and European Union, forms of fuel excise tax credit are allowed for biofuels blenders. These can claim the tax credit for the blending content of renewable fuel used in a unit of (fossil) fuel sold. Also, carbon dioxide excise tax exemption is also practised in support of biofuels use aims at protecting domestic industries through the use of tariffs on imported biofuels goods. This instrument is currently used across a number of countries or block of countries and is more or less damaging on the competitiveness of international trade.

Various support policies are nonetheless being adopted across countries to promote biofuels use. The recent Commission Directive 2009/28/EC on the promotion of energy from renewables establishes Member States' shares in renewables required by the Commission by 2020. Renewables shares as well as recent biofuels shares in 2007 (European Commission, 2009) are illustrated in Table 2.2.

Current projections (EurObserv'ER, 2009) also estimate that the European Union is near (5.3%) in reaching the target of 5.7% of renewable fuels under Commission Directive 2003/30/EC by 2010. In order to achieve the desired target, the European Union allows for certain tax measures to promote biofuels

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Country	% of energy from renewables by 2020 under Directive 2009/28/EC	% of renewable fuels by 2010 under Directive 2003/30/EC	% of biofuels in 2007	
Austria	34	5.75	4.23	
Belgium	13	5.75	1.07	
Bulgaria	16	5.75	4.82	
Cyprus	13	5.75	-	
Czech Republic	13	5.75	0.50	
Denmark	30	5.75	0.14	
Estonia	25	5.75	0.06	
Finland	38	5.75	-	
France	23	7 (2010), 10 (2015)	3.57	
Germany	18	5.75	7.35	
Greece	18	5.75	1.21	
Hungary	13	5.75	0.20	
Ireland	16	-	0.60	
Italy	17	2.50	0.46	
Latvia	40	5.75	0.14	
Lithuania	23	5.75	4.35	
Luxemburg	11	5.75	1.46	
Malta	10	_	1.08	
The Netherlands	14	5.75	2.00	
Poland	15	5.75	0.68	
Portugal	31	5.75	2.54	
Romania	24	5.75	0.79	
Slovak Republic	14	5.75	2.53	
Slovenia	25	5.75	0.83	
Spain	20	5.83 (2010)	1.11	
Sweden	49	5.75	4.00	
United Kingdom	15	5 (for transport fuels)	0.84	
EU-27	20	5.75	2.58	

#### Table 2.2 Shares of energy from renewables

Source: Directive 2009/28/EC and Directive 2003/30/EC.

use across Member States. Of particular interest are tariffs on ethanol imports. These correspond to 10.20/hl for denaturated ethanol and 19.20/hl for undenaturated ethanol. Although these measures are still seen as protectionist approaches to biofuels production (and therefore a threat to resource access) from developing countries' perspective, biofuels industries in the European Union are relatively 'new' (compared to those already in place in Brazil or United States). Furthermore, the latest European Union enlargement and the restructuring of the energy market (and that of Eastern European economies) may be seen as arguments in favour of the use of tariffs on imported biofuels commodities to promote the development of a European biofuels market. Prevalent practices across the

European Union are also those incorporating tax rates into the selling of transport fuels which are comparable to 3.5% of total fuel use in the transport sector from 2010. On average, tax rates on biodiesel and ethanol are currently 50% lower than those on diesel and gasoline.

Likewise in the United States similar measures are used to support the biofuels chain (including consumption). These can be found in the form of tax incentives for fuel-switching engine cars or quality standards on fuels. Over the last years, though, the American public support has turned its attention to third-generation biofuels (e.g. biomass/cellulose-based biofuels), sustaining numerous projects. However, at present, excise tax credits (USD 0.135/l for ethanol and USD 0.264/l for biodiesel) and import tariffs are mainly used as instruments for biofuels support across states. The support policy for biofuels in the United States tends to apply low tariffs on imported biofuels commodities. Tariffs on ethanol are for example the equivalent of 1.2–2.5% of the tariffs in countries outside NAFTA. Blending practices are also notably applied to favour the re-export of biofuels goods in particular to the European Union.

In countries, such as Brazil, China, Japan and Canada, other specific, but analogous measures, are being implemented. Brazil has for long benefitted from tax exemptions, and also blending of ethanol to fossil fuels (ranging between 20–25% of ethanol content) is regulated according to government resolutions. Biodiesel blending to diesel mandates are in the figure of two and five per cent from 2013. On the international side, Brazil applies a high tariff (e.g. 20%) on imported biofuels commodities to protect the domestic market. China has only recently supported the production of biofuels though its promotion is still going through an experimental phase. The government, on the other hand, fully supports the distribution losses across the country. Blending with other fuels (enforced at ten per cent) is in force only in few cities (i.e. around 26 in 2006), and substantial subsidies are currently in place including forms of refund for value added.

Similar to China, the Japanese experience in biofuels production is also experimental, and most policies aim at setting targets for biofuels use in the transportation sector only. Canada, on the other hand, is a step forward compared to Asian countries. Compulsory mandates for blending ethanol and biodiesel in fossil fuels range between two and five per cent content by 2012. At federal level, Canadian government is heavily supporting (CAD 2.2 billion from 2008, OECD, 2008) biofuels production and consumption with additional tax exemption measures, subsidies and import tariffs (CAD 0.05/l) on imported biofuels commodities.

## 2.5.1 Climate change mitigation policies

Agricultural practices are becoming increasingly essential for climate change because of their influential role in carbon sequestration. For example in cultivated lands carbon remains captured within the soil; if afforestation or reforestation practices are in place, carbon becomes subject of long-term sequestration as well as in the case of land or forestry rotation practices. When land is converted for fuel crops, the amount of GHG reductions depends on the net effects that the biofuels feedstock production releases on the yields (see also Section 2.3). The occurrence of positive benefits for climate change mitigation from agricultural biofuels practices is mostly not recognised by the society. On the contrary, various projects aiming at improving energy efficiency or reducing emissions generated by the industrial sector receive emission permits under the requirements of the Kyoto Protocol. Furthermore, even though the Protocol addresses carbon permits for bioenergy production, current practices to account for these mechanisms are similar to those of energy generation from grids. This leaves developing countries, where technology level is limited, incapable of contributing to GHG emission reductions and generating income from bioenergy credits. Similarly, afforestation and reforestation accounting practices for carbon payments in developing countries still remain too complex to be implemented. On the other hand, these practices have not yet been incorporated into the existing European Union Emission Trading System (ETS).

The Kyoto Protocol established three main mechanisms for carbon reductions: (1) International Emission Trading System; (2) Joint Implementation (JI) allowing carbon trading projects between developed countries and economies in transition; and (3) Clean Development Mechanism (CDM) allowing the trading of carbon reductions between developed and developing countries. The latter is an essential tool for developing countries to generate carbon credits. However, while most of current projects consist in reducing GHGs from energy efficiency, wind and solar or biomass energy projects, agricultural land-use change (including biofuels feedstock production) and afforestation and reforestation activities are not yet eligible for certified emissions in CDM. Future scenarios may be possible under post-Kyoto negotiations after 2012. These should include land-use changes (as well as afforestation and reforestation policies) to compensate countries for the carbon credits gained under land conversion for biofuels feedstock and biomass production.

Similarly, the possibility to develop a carbon trading system for bioenergy activities is under scrutiny. Brazil is moving toward the establishment of a domestic carbon market based on a cap-and-trade system for ethanol. The sugar cane industry believes that numerous advantages for the country exist (Brazil Institute, 2009). Firstly, the system would grant the industry to trade on sugar cane by-products and therefore providing opportunities to capture carbon emissions. Secondly, it would also support value-added creation encouraging the international market to purchase differentiated agricultural products and increase the supply chain worldwide. Brazil is also pushing toward an afforestation trading system to allow land-use change and forestry management to account for carbon reductions. This argument is based on Brazilian commitment to reduce deforestation by 75% by 2017 and the possibility that the United States could soon adopt a voluntary cap-and-trade mechanism on bioenergy and afforestation. The consequent

realisation of a bilateral trade between Brazil and United States on these new carbon markets would decrease carbon emissions and distribute the benefits of carbon credits from bioenergy sources across farmers.

#### 2.6 Conclusions and future trends

The present chapter was mainly aimed at presenting a discussion on several objectives of biofuels policies.

Firstly, the analysis touched on multiple effects of biofuels production and use such as the need for guaranteeing energy security and supply to an increasing number of countries currently heavily dependent on fossil fuels imports and subject to the negative effects of international fluctuations in oil prices which dramatically affect the domestic economy. Several policies and regulations are now under way in various countries to favour energy supply and safety. The European Union, for example, is moving toward a renewable energy and low carbon economy by adopting a series of directives promoting energy from renewable sources (including biofuels) or voluntary initiatives such as the 20–20–20 policy to commit to GHG emission reductions. In Brazil, the support of the electricity and heat production industries favoured the adoption of biofuels activities across country which favoured the creation of thousands of small farms. The United States is also experiencing a revision of its RFS policy allowing the country to establish biofuels targets in the future.

Secondly, bioenergy production also contributes to a number of environmental issues other than carbon (and other) emission reductions such as biodiversity, soil productivity and land-use change. A deeper analysis illustrated the effects (direct and indirect) of land conversions for biofuels feedstock production. The debate mainly concentrates on the measurement of indirect effects of land-use change and accounting practices for carbon reduction.

Thirdly, the expansion of rural areas and food safety is central to the advance in biofuels production. The nexus between rural development and bioenergy focuses on three main aspects: (1) social benefits of biofuels policies such as job and income creation having positive repercussions on rural communities; (2) public sector intervention and the progression of second-generation biofuels from non-food crops; (3) food security versus land management issues. This is at the heart of current debate on food and energy price increase. The international community through financial aid and support in technological advances plays an important role in protecting undernourished population and marginal areas in developing economies.

Fourthly, the increasing support for biofuels policies over the last years has taken place under a variety of policy tools. Subsidies to the biofuels industries have been instrumental in the international success of bioenergy practices, although the presence of distortionary effects on the society advocated by economic theory counterbalance the positive effects (on the economy and environment) arising from biofuels production. Various support policies are nevertheless being adopted across countries to promote biofuels use including capital grants, tax incentives and trade tariffs.

Finally, the agriculture and forestry conversion to bioenergy crops contributes to climate change mitigation. Currently, positive benefits of climate change mitigation from agricultural biofuels practices are not recognised within international climate change agreements such as the Kyoto Protocol. This would leave developing countries, where technology level is limited, incapable of contributing to carbon reductions and generating income from bioenergy credits. The scope for creating cap-and-trade systems for bioenergy crops and afforestation and reforestation programmes is on the way (in the United States and Brazil) for two reasons: to incentivise sugar cane industry to sell carbon emissions credits and to favour the creation of value added. This would support the international diversification of carbon markets and help distributing the benefits of carbon credits from bioenergy sources in agricultural and rural areas.

With regard to future trends, several scenarios can be delineated for multiple objective policy approaches for biofuels production. Advances in technological research and development and learning processes from past and current experiences (i.e. international food and oil price increases, land management competition for food and biofuels feedstock debate) indicate that one of the main pathways toward a long-term sustainability of the human and natural environment is a bio-based economy. The European Union, United States and a number of other countries have recognised, through recent regulation, that a substantial reduction in oil and petroleum products should be adopted in order to face increasing demand for energy and mitigate climate changes at the same time.

The European Union, for example, is aiming at achieving a reduction of 20% of carbon emissions by 2020 with increasing use of renewable sources by 20%. It is an ambitious policy given the current economic crisis and unemployment pressures and restructuring of the economy in new Member States. Nonetheless, the European Union is moving toward an energy-efficient market with ample space for the implementation and diffusion of biofuels technologies and products to renovate the agricultural sector and promote bio-refineries installations. The United States, on the other hand, is currently experiencing a revision of its RFS policy. The adoption of a strategic approach at all levels of the biofuels production chain would ensure coordinated measures: across governmental departments and agencies in view of economic, environmental and social concerns; and between research and commercialisation phases to converge a multitude of stakeholders' needs. Also, monitoring the implementation of biofuels projects would result in further advantages for the entire biofuels supply industry.

Efficiency in strategic planning is also claimed to improve the quantification of indirect effects of biofuels production and use. These may come in the form of displacement effects of fossil fuels emissions gained over new lands for bio-crop production which are not taken into account in current carbon reduction inventories. Furthermore, intergenerational issues (such as discounting rates and

time management) are also relevant for valuing life-time effects of biofuels plants over different generations and natural resource use.

Efficient management of biofuels production also aims at rural development in developing countries. The Brazilian experience is a unique case where strong market integration (across the sugar cane industry, electricity supply and transport sector, for example) and transparent institutional framework have favoured the launch of biofuels production. Replication of this mechanism, including the lessons from Brazil's learning-by-doing experiences, elsewhere becomes essential to promote agricultural growth, income generation and biodiversity protection in developing economies.

It is essential at this stage of the biofuels chain development to sustain technology advances for second- and third-generation biofuels (i.e. lignocellulosic). This would aim at reducing current land competition between food and non-food crops. Current support for research is therefore a strategic element toward worldwide reduction in food and energy prices. The European Union, the World Bank and the United States agree that enhancing continuous support to research and development for next-generation biofuels would serve as a key factor to favour the improvement of current international food crisis, energy dependence and carbon emission reductions. From a developing countries' perspective (granted that new forms of biofuels technologies are being implemented locally through international financial support) this would also help in reducing the dependence on foreign markets in food and energy. A number of macroeconomic positive impacts would follow such as improving balance of payment accounts, boosting employment and income generation and reducing the gap in poverty conditions. However, enhancing agricultural activities and new forms of biofuels locally would not have expected positive effects if the international community does not apply reductions in trade tariffs on biofuels commodities. Efforts in this direction become essential in particular for improving the functioning of international agreements (e.g. the Doha Round) affecting agricultural markets (World Bank, 2008).

Support policies for the biofuels industry are crucial for the development of new markets for bio-commodities. Though governmental subsidies are playing an important role in supporting bio-crops production, these nonetheless generate distortionary effects when used for unproductive reasons. Government aid is therefore called for implementing alternative incentivising mechanisms to ensure adequate measures for land conversion. Long-term forms of investment grant (either from public or private sources) subject to continuous monitoring of land management practices would guarantee the efficiency of bio-based projects and avoid waste of financial resources.

Land-use practices for bioenergy production are vital to mitigate climate change. Land conversions for fuel feedstock would produce net benefits to the society (in terms of carbon emission reductions) which are not fully internalised in social well-being. Post-Kyoto negotiations should address land-use changes to compensate countries for the credits gained from carbon emission reductions. There exists a possibility to develop a carbon trading system for bioenergy commodities. Brazil is moving toward a cap-and-trade mechanism for ethanol, and voluntary agreements are under way with the United States to adopt a bilateral trade market for carbon credits from bioenergy sources and afforestation activities. This would not only guarantee the creation of value added for the domestic economy, but also serve as attraction to foreign investors to invest in agricultural activities in support of a bio-based economy.

## 2.7 List of selected economies in Fig. 2.1 and 2.2, and Tables 2.1 and 2.2

Emerging and developing economies:

Afghanistan, Republic of Albania, Algeria, Angola, Antigua and Barbuda, Argentina, Armenia, Azerbaijan, Bahamas, The Bahrain, Bangladesh, Barbados, Belarus, Belize, Benin, Bhutan, Bolivia, Bosnia and Herzegovina, Botswana, Brazil, Brunei Darussalam, Bulgaria, Burkina Faso, Burundi, Cambodia, Cameroon, Cape Verde, Central African Republic, Chad, Chile, China, Colombia, Comoros, Congo, Democratic Republic of Congo, Republic of Costa Rica, Côte d'Ivoire, Croatia, Djibouti, Dominica, Dominican Republic, Ecuador, Egypt, El Salvador, Equatorial Guinea, Eritrea, Estonia, Ethiopia, Fiji, Gabon, Gambia, The Georgia, Ghana, Grenada, Guatemala, Guinea, Guinea-Bissau, Guyana, Haiti, Honduras, Hungary, India, Indonesia, Iran, Islamic Republic of Iraq, Jamaica, Jordan, Kazakhstan, Kenya, Kiribati, Kuwait, Kyrgyz Republic, Lao People's Democratic Republic, Latvia, Lebanon, Lesotho, Liberia, Libya, Lithuania, Former Yugoslav Republic of Macedonia, Madagascar, Malawi, Malaysia, Maldives, Mali, Mauritania, Mauritius, Mexico, Moldova, Mongolia, Montenegro, Morocco, Mozambique, Myanmar, Namibia, Nepal, Nicaragua, Niger, Nigeria, Oman, Pakistan, Panama, Papua New Guinea, Paraguay, Peru, Philippines, Poland, Qatar, Romania, Russia, Rwanda, Samoa, São Tomé and Príncipe, Saudi Arabia, Senegal, Serbia, Seychelles, Sierra Leone, Solomon Islands, South Africa, Sri Lanka, St. Kitts and Nevis, St. Lucia, St. Vincent and the Grenadines, Sudan, Suriname, Swaziland, Syrian Arab Republic, Tajikistan, Tanzania, Thailand, Timor-Leste, Democratic Republic of Togo, Tonga, Trinidad and Tobago, Tunisia, Turkey, Turkmenistan, Uganda, Ukraine, United Arab Emirates, Uruguay, Uzbekistan, Vanuatu, Venezuela, Vietnam, Yemen, Republic of Zambia, and Zimbabwe

Advanced economies:

Australia, Austria, Belgium, Canada, Cyprus, Czech Republic, Denmark, Finland, France, Germany, Greece, Hong Kong SAR, Iceland, Ireland, Israel, Italy, Japan, Korea, Luxembourg, Malta, Netherlands, New Zealand, Norway, Portugal, Singapore, Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Taiwan Province of China, United Kingdom, and United States

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## Life cycle sustainability assessment of biofuels

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Abstract: Biofuels have a potential to reduce carbon dioxide emissions from transport because the biomass used in their production is considered carbon neutral. This is the main reason for a growing interest in biofuels. However, there are certain aspects, particularly of the first-generation biofuels, which may render them unsustainable, including the increased use of land and competition with food production. Therefore, sustainability of biofuels should be assessed carefully, considering all relevant environmental, economic and social aspects. To prevent shifting the impacts along the supply chains, sustainability should be assessed considering the whole life cycle of biofuels, including cultivation of the feedstock and biofuel production processes. This chapter reviews various sustainability aspects of biofuels and illustrates how environmental and economic sustainability can be assessed on a life cycle basis. The environmental impacts considered include water use, global warming, acidification, eutrophication and loss of biodiversity while economic aspects include feedstock costs, capital costs and biofuel prices. Future viability of biofuels is also discussed.

**Key words:** biofuels, environmental impacts, economic costs, life cycle assessment, sustainability assessment.

## 3.1 Introduction

Biofuels can be produced from a range of biomass sources using different production routes, as discussed throughout this book. Depending on the type of the bio-feedstock used, they are referred to as first-, second- or third-generation biofuels (OECD and IEA, 2008). First-generation biofuels are produced commercially from conventional food crops, including wheat, maize, corn, sugar cane, rapeseed, sunflower seeds and palm oil. The most common first-generation biofuels are bioethanol, biodiesel, vegetable oil and biogas.

Second-generation biofuels are produced from non-food sources and include dedicated energy crops (e.g. perennial grasses, short-rotation coppice willow and other lignocellulosic plants) and waste biomass (e.g. agricultural, forestry and municipal solid waste). Two main processing routes used to produce these fuels are: thermo-chemical and bio-chemical. The former is used mainly for the production of biodiesel and the latter for bioethanol. Other second-generation fuels under development include: biohydrogen, biomethanol, dimethylfuran (DMF), bio-dimethylether (bio-DME), Fischer-Tropsch diesel, biohydrogen diesel and mixed alcohols (Brigenzu *et al.*, 2009).

Third-generation biofuels are still under development and the main biofeedstock being considered are algae for the production of biodiesel via the thermo-chemical route. Other sources of third-generation biofuels could include alcohols such as bio-propanol or bio-butanol; however, they are not expected to enter the market before 2050 (OECD and IEA, 2008).

Currently, the majority of the global biofuel production is from food crops with bioethanol representing over 80% of liquid biofuels by energy content (Brigenzu *et al.*, 2009); however, the importance of the second- and third-generation fuels is growing.

Biofuels have a potential to reduce the carbon dioxide  $(CO_2)$  emissions because the biomass used in their production is considered carbon neutral. This is based on the assumption that the amount of carbon released during combustion of biofuels in the use phase is equivalent to the amount of carbon sequestered during the growth of biomass from which the fuels were derived. Further attractive features of biofuels over fossil fuels are that they provide security of supply as they can be produced domestically by many countries. Furthermore, they require only minimal changes in the distribution system and production technologies. Biofuels also have a potential to stimulate rural development (Rajagopal and Zilberman, 2007). Thus, the expectations from biofuels as a source of 'sustainable' energy are high.

However, there are certain aspects, particularly of the first-generation biofuels, which may render them less sustainable. For example, while the intensification of agriculture to increase crop production per land unit may lead to lower greenhouse gas (GHG) emissions per unit of product, the increased use of land, energy, fertilisers and pesticides will reduce the net GHG benefits and cause further environmental damage, including release of soil carbon, leaching of nutrients and loss of biodiversity. Other risks associated with large-scale production of the first-generation biofuels include competition with food production, leading to increased costs of food and in some cases, food poverty (Bird *et al.*, 2008; Escobar *et al.*, 2009; Fargione *et al.*, 2008; Searchinger *et al.*, 2008).

Therefore, sustainability of biofuels should be assessed carefully, considering all relevant environmental, economic and social aspects (The Royal Society, 2008). Furthermore, to prevent shifting the burdens along the supply chains, sustainability should be assessed taking a systems approach and considering the whole life cycle of biofuels, including cultivation of the feedstock and biofuel production processes (Azapagic, 2006; Fehrenbach *et al.*, 2007; Stichnothe and Azapagic, 2009; The Royal Society, 2008; US EPA, 2009). The life cycle approach is also required by various legislative acts related to biofuels, including the European Union (EU) Renewable Energy Directive (EC, 2009), the German Sustainability Biofuel Ordinance (GFG, 2007), the Swiss Directive on Mineral Oil Tax Redemption for Biofuels (SFG, 2007), the UK Renewable Transport Fuel Obligation (DfT, 2008) and the US Energy Independency and Security Act (USFG, 2007).

This chapter discusses how the main sustainability issues associated with biofuels can be assessed on a life cycle basis, considering different bio-feedstocks and production routes.

# 3.2 Sustainability issues along the life cycle of biofuels

As shown in Fig. 3.1, the life cycle of biofuels encompasses planting, growing and harvesting of biomass (if applicable), conversion to the biofuel and its use, also including all transportation steps used in the system. Each stage in the life cycle is associated with several sustainability issues, depending on the type of the feedstock and biofuel. Some of these issues are listed in Table 3.1 (Brigenzu *et al.*, 2009; IDB, 2009; The Royal Society, 2008). Several of the environmental and social issues, particularly those associated with land use, food security and health impacts, have been discussed in chapter 2. Here, the focus is on the life cycle environmental impacts and economic costs.



3.1 The life cycle of biofuels from 'cradle to grave'. T: transport.

Environmental	Economic	Social
<ul> <li>Global warming (GHG emissions)</li> <li>Land availability</li> <li>Land-use change</li> <li>Biodiversity</li> <li>Water consumption</li> <li>Other environmental impacts</li> </ul>	<ul> <li>Feedstock costs</li> <li>Investment costs</li> <li>Biofuel price</li> <li>Local income generation</li> </ul>	<ul> <li>Human health</li> <li>Human and labour rights</li> <li>Land ownerships</li> <li>Impact on food security</li> <li>Community development</li> <li>Impact on indigenous peoples</li> </ul>

Table 3.1 Some sustainability issues in the life cycle of biofuels

Note: The issues are not identified by life cycle stage as many apply to several stages or the whole life cycle.

Source: Brigenzu et al. (2009), IDB (2009) and The Royal Society (2008).

## 3.3 Environmental sustainability of biofuels

Life cycle assessment (LCA) is used as the main tool for evaluating the environmental sustainability of biofuels on a life cycle basis. A brief overview of the LCA methodology can be found in the Appendix. The following sections discuss the global warming potential (GHG emissions) and other environmental impacts of biofuels produced from different feedstocks.

## 3.3.1 Global warming (GHG emissions)

Estimation of GHG emissions from biofuels has been the subject of many studies internationally, in an attempt to evaluate what savings, if any, can be achieved over the fossil-based fuels. This has required significant methodological developments to ensure that the biofuels and fossil fuels are compared on an equivalent basis. These include defining an equivalent unit of analysis (functional unit) and system boundaries as well as an appropriate allocation method (see the Appendix for the definitions of the terms).

The life cycle of fossil fuels, with the system boundary equivalent to that of the biofuels system given in Fig. 3.1, encompasses the extraction of crude oil, the transportation to the refinery, all refinery processes to produce petrol and diesel and the use of the fuels. This is illustrated in Fig. 3.2. As in the biofuels system, all material and energy inputs into the system and emissions and wastes from the system are included in the system boundary.

The equivalent unit of analysis for comparison is based on the equivalent energy content of the fuels and usually defined (arbitrarily) as '1 MJ of fuel'. The global warming potential (GHG emissions) is expressed either in g or kg  $CO_2$  eq./ MJ and the GHG savings from biofuels compared to the fossil fuels are calculated as (DfT, 2008):

$$GHG_{saving} = \frac{GHG_{fossil \, fuel} - GHG_{biofuel}}{GHG_{fossil \, fuel}} \times 100 \quad (\%)$$
[3.1]



*3.2* The life cycle of fossil fuels, used as a reference system for comparison with biofuels.

Different countries use different reference values for fossil fuels and the approaches to estimating the GHG emissions from biofuels. A selection of these approaches is summarised in Table 3.2. In the EU countries, the different national approaches will be synchronised with the EU Renewable Energy Directive (RED) by 2011. Some of the methodological issues such as allocation of environmental impacts and land-use change are discussed further below. Prior to that we compare the GHG emissions of different biofuels from different feedstocks and country of origin.

Figure 3.3 compares GHG emissions of bioethanol and biodiesel from different feedstocks cultivated in different countries with conventional fuels. Using 1 MJ

	Germany (Fehrenbach <i>et al.,</i> 2007)	UK (DfT, 2007)	Holland (Bindraban <i>et al.,</i> 2009)	EU RED (EC, 2009)	US (US EPA, 2009)
Base year	N/A	2005	2005	2008	2005
Reference value for diesel (g $CO_2$ eq./MJ)	86.2	86.4	N/A	Most recent value or	N/A
Reference value for petrol (g $CO_2$ eq./MJ)	85.0	84.8	N/A	83.8	N/A
System boundary	Cradle to grave	Cradle to grave	Cradle to grave	Cradle to grave	Cradle to grave
Capital goods/ infrastructure	Excluded	Excluded	Excluded	Excluded	Excluded
Pesticides	Included	Included	Excluded	Included	Included
Fertilisers	Included	Included	Partly included <sup>1</sup>	Included	Included
Allocation method	Net calorific value	System expansion	System expansion	Net calorific value	System expansion/ economic value <sup>2</sup>
Direct land-use change	Included (IPCC, 2007)	Included (IPCC, 2007)	Included (IPCC, 2007)	Included (IPCC, 2007)	Included (IPCC, 2007)
Indirect land-use change	Excluded	Excluded	Excluded	Excluded	Included
GHG saving threshold (%)	30–40 <sup>3</sup>	40–50 <sup>4</sup>	30	35–60 <sup>5</sup>	20–60 <sup>6</sup>

Table 3.2 Overview of the GHG calculation methodologies for biofuels in different countries

N/A - not available.

<sup>1</sup>N-fertilisers are included but P- and K-fertilisers are excluded. <sup>2</sup>The allocation procedure used depending on the system. <sup>3</sup>40% after 2012. <sup>4</sup>45% in 2009–10 and 50% after 2011. <sup>5</sup>50% in 2017 and 60% thereafter. <sup>6</sup>20% on average for all renewable fuels; 50% for biodiesel and 60% cellulosic ethanol.



*3.3* Greenhouse gas emissions from biofuels compared with conventional transport fuels (DfT, 2007; Stichnothe and Azapagic, 2009).

as the basis for comparison, the best performing biofuel from food crops is ethanol from sugar cane, offering a GHG saving of 70% over petrol (DfT, 2008). However, overall the best biofuel is ethanol from biological waste (derived from municipal solid waste) offering a saving of 90% (Stichnothe and Azapagic, 2009). Furthermore, biofuels from waste do not compete for land; on the contrary, using non-recyclable waste as a resource saves the landfill disposal capacity, supports the re-use of resources and leads to a reduction of GHG emissions from disposal sites (Stichnothe and Azapagic, 2009).

On the other hand, ethanol from US corn does not appear to offer any GHG savings over petrol; in fact its overall GHG emissions are higher than that of petrol. However, these results depend on the assumptions used in the estimation of the GHG emissions. As shown in Fig. 3.4 and Fig. 3.5 (DfT, 2008; Edwards *et al.*, 2008; Fehrenbach *et al.*, 2007), the results vary considerably, depending on the production routes and allocation procedures (see the Appendix and Section 'Allocation of environmental impacts' for the latter). Taking these variations into account, bioethanol from sugar cane is still the best performing fuel offering an average GHG saving of approximately 60%. The average savings for biodiesel are closer together for all four feedstocks shown in Fig. 3.5, although it would appear that soybean can achieve highest savings at the top-end performance.

#### Allocation of environmental impacts

The definition of the term 'allocation' and the allocation methods used in LCA are given in the Appendix. The allocation issue arises in systems where biofuels are co-produced with other outputs, such as electricity and/or heat so that the impacts have to be allocated between the co-products in an appropriate way. As shown in Table 3.2, most international approaches favour either allocation based on energy



*3.4* GHG savings for bioethanol from different feedstocks and country of origin (DfT, 2009; Edwards *et al.*, 2008; Fehrenbach *et al.*, 2007).

content (net calorific value) or system expansion. In the latter, the system is credited for producing the additional output. However, the methodological difficulty is in identifying the 'correct' way to credit the system. For example, if the electricity is co-produced with the biofuel in an EU country, the question is what electricity mix should be used to credit the system: best available technology, the average national or EU energy mix? The choice of the allocation method and the 'credit' are of the utmost importance as often very different results are obtained using different approaches. In any case, this should be examined as part of the sensitivity analysis (see the Appendix and the textbox).

The EU RED (EC, 2009) favours allocation based on the energy content of biofuels, although other allocation procedures, such as system expansion or



*3.5* GHG savings for biodiesel from different feedstock and country of origin (DfT, 2007; Edwards *et al.*, 2008; Fehrenbach *et al.*, 2007). For legend, see 3.4.

economic value might be more appropriate in particular cases. For example, energy allocation cannot be applied in systems where biofuel co-products do not have an energy value but have an economic value, e.g. ash and fertilisers. In these cases, allocation based on the economic value may be more appropriate. However, this produces volatile results in line with economic values of commodities and should be used only where other allocation methods cannot be applied (ISO, 2006b).

An example of how to allocate environmental impacts using two different bases – mass and energy – can be found in the textbox on pages 46–47.

#### Land-use change

Land-use change (LUC) is probably the most controversial issue associated with biofuels (Fargione *et al.*, 2008). The main concern is related to possible additional GHG emissions when carbon stored in the soil is disturbed and released as  $CO_2$  due to the LUC. Two types of LUC are considered: direct and indirect. Direct LUC involves the conversion of existing land from a current use to the cultivation, in this instance, of biomass feedstocks for biofuel production. As shown in Table 3.2, direct LUC is considered in most international approaches and the IPCC factors are used for these purposes (IPCC, 2007). These are summarised for selected countries in Table 3.3.

Country	Current land use	Previous land use	GHG emissions (t CO <sub>2</sub> eq./ha.yr)
Australia	Annual cropland	Forest land	23
		Grassland	2.2
	Perennial cropland	Forest land	21
		Grassland	1.9
Brazil	Annual cropland	Forest land	37
		Grassland	10.3
	Perennial cropland	Forest land	26
<b>A</b>		Grassland	8.5
Canada	Annual cropland	Forest land	17
	р	Grassland	2.2
	Perennial cropland	Forest land	16
-		Grassland	1.9
France	Annual cropland	Forest land	18
		Grassland	4.5
	Perennial cropland	Forest land	14
0		Grassland	4.2
Germany	Annual cropland	Forest land	21
		Grassland	/
	Perennial cropland	Forest land	14
		Grassland	6.7
Indonesia	Annual cropland	Forest land	33
		Grassland	19.5
	Perennial cropland	Forest land	31
		Grassland	17.7
Malaysia	Annual cropland	Forest land	3/
		Grassland	10.3
	Perennial cropland	Forest land	26
D 1		Grassland	8.5
Pakistan	Annual cropland	Forest land	16
		Grassland	3.6
	Perennial cropland	Forest land	15
0 11 47 1		Grassland	3.2
South Africa	Annual cropland	Forest land	26
		Grassland	1.6
	Perennial cropland	Forest land	25
		Grassland	1.2
United Kingdom	Annual cropland	Forest land	2/
		Grassland	7.0
	Perennial cropland	Forest land	20
		Grassland	6./
USA	Annual cropland	Forest land	1/
	Demonstrations and the	Grassiand	1.9
	Perennial cropland	Forest land	
		Grassiand	1.5

Table 3.3 GHG emissions related to direct land-use change for selected countries

Source: IPCC (2007).

Indirect LUC is associated with the displacement of existing agricultural activity (Searchinger *et al.*, 2008). This is often difficult to assess due to the uncertainties involved, particularly at the international level. Currently, only the US approach considers indirect land-use change (US EPA, 2009).

An illustration of the influence of direct LUC for biodiesel from rapeseed is given in Table 3.4. Based on the assumptions used in this example (Fehrenbach *et al.*, 2007), biodiesel from rapeseed can provide GHG savings of 48% compared to diesel. However, if direct LUC occurs, the saving drops to below ten per cent. Given that most countries require significantly higher GHG savings (see Table 3.2), it is important to ensure that biofuels can still meet these requirements if LUC is involved.

	GHG emissions	GHG savings
	(g CO <sub>2</sub> eq./MJ)	relative to diesel (%)
Total without LUC	45.2	_
Direct LUC	32.8 <sup>1</sup>	47.5
Total with LUC	78.0	9.5

*Table 3.4* The influence on the GHG emissions with and without direct-land change use for biodiesel from rapeseed oil

<sup>1</sup>Assumes worst case – conversion of land with high carbon content. Source: Fehrenbach *et al.* (2007).

#### Textbox

#### Allocation of GHG emissions - An example

The example process chosen for illustration is transesterification of rapeseed oil to produce rapeseed oil methylester (RME) as the main product and glycerine as a co-product. Therefore, the environmental impacts have to be allocated between these two products, using an appropriate allocation basis. Two allocation approaches are considered here – mass and energy basis – to illustrate the difference in the approach as well as any difference in the LCA results. GHG emissions are used for illustration purposes. This example is based on that found in Fehrenbach *et al.* (2007).

The process produces 1 kg of RME and 0.092 kg of glycerine. The total GHG emissions from the process are 0.307 kg  $CO_2$  eq. The lower heating value (LHV) of RME is 37.2 MJ/kg and of glycerine is 17 MJ/kg.

1. Mass-based allocation:

Total I	mass of	products i	n the process:	1 k	g RME	+ 0.092	kg	glycerine =	- 1.0	)92 kg
					J			5.7.5.5.1.5		

Allocation factor: RME: Glycerine:

1 kg/1.092 kg × 100 = 91.6% 0.092 kg/1.092 × 100 = 8.4%

Therefore, 91.6% of GHG emissions are allocated to RME and 8.4% to glycerine so that:							
GHG emission	ns allocated to RME:	0.307 kg $CO_2$ eq. × 0.916 = 0.28 kg $CO_2$ eq.					
GHG emission	ns allocated to glycerine:	0.307 kg CO <sub>2</sub> eq. × 0.084 = 0.027 kg CO <sub>2</sub> eq.					
2. Energy-con	tent based allocation						
Total energy c 37 MJ/kg × 1 I	ontent of RME and glyce kg RME + 17 MJ/kg × 0.0	erine based on their respect 92 kg glycerine = 38.76 MJ	ive LHVs:				
Allocation fac RME: Glycerine:	Allocation factor:       (37 × 1)/38.76 × 100       = 96%         Glycerine:       (17/0.0.092)/38.76 × 100       = 4%						
Therefore, 969 so that:	Therefore, 96% of GHG emissions are allocated to RME and 4% to glycerine so that:						
GHG emissior	GHG emissions allocated to RME: 0.307 kg $CO_2$ eq./38.76 MJ × 1000 GJ × 0.96 = 7.6 kg $CO_2$ eq./GJ RME						
GHG emissior	GHG emissions allocated to glycerine: 0.307 kg $CO_2$ eq./38.76 MJ × 1000 GJ × 0.04 = 0.32 kg $CO_2$ eq./GJ glycerine						
Converting these back to per mass output from the process, the GHG emissions allocated to:							
RME:	RME: $7.6 \text{ kg CO}_2 \text{ eq./GJ RME} \times 38.76 \text{ MJ/1000 GJ} = 0.29 \text{ kg CO}_2 \text{ eq.}$						
Glycerine:	0.32 kg CO <sub>2</sub> eq./GJ RM	E × 38.76 MJ/1000 GJ = 0.0	12 kg CO <sub>2</sub> eq.				
Comparing these to the mass allocation, the results for RME are similar but by a factor of two different for glycerine. Although arguably in the example presented here, the differences in the results due to the different allocation methods are small, in many cases they can be much larger and can affect the LCA results significantly. It is therefore important that sensitivity analysis is carried out to determine the influence on the results of different allocation methods.							

In addition to LUC, different crop management practices can also influence emissions of carbon from soil. However, there is still considerable uncertainty and lack of knowledge regarding the loss from or sequestration of carbon in soils due to this. It is also unclear how temperature increase due to climate change might alter farm management practices (and other activities) and what effect that will have on the change of carbon in soils (Baker *et al.*, 2007; Bellamy *et al.*, 2005; Davidson and Janssens, 2006).

A recent study in the UK found that the Soil Organic Carbon (SOC) stocks are being depleted at an alarming rate due to a combined effect of these factors. The

measurements of SOC on 6000 sites across all types of land use over the past 25 years have shown that the estimated annual losses of carbon are equal to 13 million tonnes. This is equivalent to eight per cent of the UK emissions of  $CO_2$  in 1990 and as much as the entire UK reduction in  $CO_2$  emissions achieved between 1990 and 2002 (Bellamy *et al.*, 2005).

It is widely believed that soil disturbance by tillage was a primary cause of the historical loss of SOC in North America. It is also believed that substantial SOC sequestration can be accomplished by changing from conventional ploughing to less intensive methods known as conservation tillage (Baker *et al.*, 2007). However, some studies have demonstrated that conservation tillage leads to higher concentrations of SOC near the surface while conventional tillage accrues more SOC in deeper soil layers. Long-term measurements have also been unable to detect carbon gain in soil due to reduced tillage. Overall, although there are other good reasons to use conservation tillage, there is no proven evidence that it promotes carbon sequestration in soil (Baker *et al.*, 2007).

Similarly, adding fresh organic matter (e.g. crop residues, compost, livestock manure and green manure) is widely practised as a way of increasing the nutrient levels in soils. However, there is also evidence that this may stimulate microbiological activity in the soil and can lead to the decomposition of ancient carbon buried in deep soil layers (Davidson and Janssens, 2006).

## 3.3.2 Other environmental impacts

The following sections provide a brief discussion of other environmental impacts that in addition to global warming are associated with biofuel systems:

#### Biodiversity

Agriculture and forestry have been the main drivers for biodiversity loss globally. For example, more land was converted to cropland over 30 years between 1950 and 1980 than over 150 years between 1700 and 1850 (MEA, 2005). Therefore, there is also a potential for biofuel crops to alter local habitats and resources in a way that will affect native species. These effects will depend on the crop, its density, duration and distribution on the landscape and any regular inputs, including water and chemicals (The Royal Society, 2008). Biodiversity loss can also occur due to direct effects of land-use change. For example, if set-aside land in Europe is used to grow biofuel crops, impacts on biodiversity will need to be evaluated because some of these areas are more biodiverse than farmlands (Critchley and Fowbert, 2000). Intensified cultivation of biofuel crops could also lead to new pests and diseases which could in turn lead to increased use of pesticides/herbicides, causing further environmental damage.

Introducing new, particularly more invasive, species into an area could lead to the displacement of local biodiversity. Eucalyptus, some Miscanthus species and switchgrass all exhibit some features of invasiveness (The Royal Society, 2008).

However, there is also some evidence that under certain circumstances biodiversity could increase. For example, large-scale short rotation coppice (SRC) such as willow can provide benefits for some bird species, butterflies and flowering plants (Anderson and Fergusson, 2006).

Therefore, it is important that the overall risks and benefits for biodiversity be evaluated appropriately for bioenergy feedstocks. The Royal Society (2008) recommends using a risk assessment framework that covers the following:

- the full life cycle of biofuel production;
- the invasiveness potential of the crop;
- potential interactive effects of the biofuel crop with other pressures in the area (e.g. drought stress);
- the impacts on ecosystems; and
- changes in these risks under a future climate.

However, the lack of data represent a significant barrier in addressing biodiversity on a life cycle basis as biofuel crops have not yet been assessed for their impacts on biodiversity. Furthermore, currently there is no agreed methodology on estimating the impacts on biodiversity in LCA.

#### Water use

Water is used throughout the life cycle of biofuels, from feedstock to biofuel production. However, water use is usually not included in LCA or other evaluations of environmental sustainability of biofuels. The main reasons are the lack of data and an agreed methodology for estimating the water footprint. Although there are some data available on water use for crops, water requirements through the rest of the supply chain are not available. This is not an issue specific to biofuels only but also to other systems – as water has started to become a global issue only relatively recently, the need for information on water consumption in different productive systems has only come to light recently. Consequently, no current LCA databases contain reliable data on water usage on a life cycle basis.

#### Other impacts

Most LCA studies of biofuels focus on GHG emissions and energy balances. However, as already discussed, biofuels have wider environmental impacts, including resource depletion, biodiversity, acidification, eutrophication and toxicity. These have rarely been considered in LCA studies to date.

As an illustration, Fig. 3.6 compares the selected environmental impacts from bioethanol (from wheat) and petrol. Global warming potential is also shown.



3.6 Environmental impacts of petrol and bioethanol. Note: Bioethanol is from wheat cultivated in Germany; comparison is made on the basis of the equivalent energy content in petrol and bioethanol; the unit of analysis is 1 litre of petrol and 1.6 litres of bioethanol (due to the lower energy content of bioethanol compared to petrol); the impacts are expressed per litre for petrol, per 1.6 litre for bioethanol; system boundary is from 'cradle to grave' (use stage not included except for GWP); DCB – dichlorobenzene.

These results illustrate that, while biofuels can provide GHG savings, their wider impacts can be higher than that of conventional fossil fuels. For the example considered here, bioethanol has three times higher acidification and 27 times higher eutrophication than petrol (note that the use stage of fuels is not considered). These are mainly due to the use of fertilisers and fuel in the agricultural machinery. Its terrestrial toxicity is 1.6 times higher, again mainly due to the assumed use of synthetic fertilisers.

From this and the earlier discussion, it is clear that evaluation of environmental sustainability of biofuels should involve consideration of all relevant environmental impacts along the whole life cycle to avoid shifting the burdens and making unsustainable choices.

We now turn our attention to the economic sustainability of biofuels.

## 3.4 Economic sustainability of biofuels

While studies on GHG emissions from biofuel systems abound, economic assessments are still rare and difficult to compare due to different assumptions for feedstocks and conversion technologies (Bridgwater, 2009). Economic data is not
available in the public domain due to confidentiality as the conversion technologies are still under development. Nevertheless, several sources provide estimates of the economic viability of biofuel systems as discussed below:

On a life cycle basis, the costs of biofuels are mainly contributed by:

- the costs of feedstock cultivation, preparation and delivery;
- the capital costs for manufacturing plants for conversion into biofuels;
- other costs such as labour, utilities, maintenance, insurance, etc.

The following sections give an overview of the feedstock and capital costs and discuss how they influence final biofuel prices.

# 3.4.1 Feedstock costs

The current costs of providing biomass in Europe vary greatly depending on the biomass and range from  $\notin 21$  to  $\notin 180$  per tonne of dry matter (DENA, 2006). The variation is due to the different energy and moisture content as well as the origin of the feedstocks. Wood chips are at the upper end of the price range while waste wood and agricultural residues are at the lower end; the average feedstock costs are  $< \notin 60$  per tonne of dry matter. These costs include feedstock storage close to the field or forest (10 km) but not the transport costs to the processing plant. The delivery costs increase with the moisture content and transportation distance.

Table 3.5 shows a breakdown of the total costs of the feedstock for the example of switchgrass in the US (US EPA, 2009). As shown, just over half of the costs

	Amount	Contribution (%)
Farm size (acres)	400	
Quantity of switchgrass (t)	1 891 000	
Farmer/grower (\$/t)	10	12.96
Nutrient replacement (\$/t)	11.81	15.31
Shredding (\$/t)	4.80	6.22
Raking (\$/t)	3.95	5.12
Baling (\$/t)	10.84	14.05
Hauling to farm edge (\$/t)	2.81	3.64
Total farm costs (\$/t)	44.20	57.29
Hauling to storage (\$/t)	15.30	19.83
Storage (\$/t)	7.89	10.23
Hauling to ethanol plant (\$/t)	9.76	12.65
Total field to plant (\$/t)	32.95	42.71
Total (\$/t)	77.15	100.00

*Table 3.5* Summary of costs for production and delivery of switchgrass in the USA

Source: US EPA (2009).

(57%) are related to the cultivation of the feedstock and the rest are due to the storage and delivery to the ethanol plant. These costs compare well with forest residue costs (US EPA, 2009).

## 3.4.2 Capital costs

Estimates of capital costs for biofuel plants (or any other developing technology) are uncertain due to the many influencing factors. An example is the 18 million litres/yr CHOREN bioethanol plant whose costs escalated from €500 million in early 2007 to €1000 million in early 2008 (Bridgwater, 2009). Nevertheless, several estimates are available for different biofuel technologies. One of the most comprehensive and consistent studies currently available, carried out by DENA (2006), puts the cost of thermo-chemical plants between €525 and €650 million for plants treating 1 million tonnes of wet biomass and producing 105000–120000 tonnes of biofuel per year. In addition to the economic benefits, this option provides operational and organisational synergies and significantly lowers the plant availability risk. Integration into an existing refinery or chemical plant can also accelerate the planning procedure and can lower investment costs by around 25% (DENA, 2006).

Table 3.6 shows the process options considered, and Table 3.7 shows the breakdown of costs. Processing route 1 appears to be economically the most sustainable option.

	Mechanical treatment	Thermal pre-treatment	Gasification	Gas purification	Synthesis	Product conditioning
Decentralised 1	Centralised Milling		Entrained- flow gasification	Gas purification	FT synthesis	Product conditioning
Decentralised 2	Shredding	Fast pyrolysis	Centralised Entrained- flow gasification	Gas purification	FT synthesis	Product conditioning
Decentralised 3	Shredding		Fluidised bed gasification	Gas purification	Methanol synthesis	Centralised Product conditioning
Decentralised 4	Shredding	Centralised Pyrolysis	Entrained- flow gasification	Gas purification	FT synthesis	Product conditioning
Decentralised 5	Shredding	Centralised Pyrolysis	Entrained- flow gasification	Gas purification	Methanol synthesis	Product conditioning

Table 3.6 Process options considered in the DENA study

Source: DENA (2006).

It is interesting to note that integration into an existing refinery or chemical plant is the most cost-effective option across the different processing routes. In addition to the economic benefits, this option provides operational and organisational synergies and significantly lowers the plant availability risk. Integration into an existing refinery or chemical plant can also accelerate the planning procedure and can lower investment costs by around 25% (DENA, 2006).

Even fewer estimates are available for the capital costs of bio-chemical plants. A recent study by the US EPA (2009) estimates the costs for a bio-chemical plant producing 56 million gallons/yr of ethanol from 849 385 dry tonnes/yr of corn stover at \$133 million/yr (for the year 2010). With other costs added (including site development, project contingency, etc.), the total project investment costs are estimated at \$232 million/yr (US EPA, 2009). For the years 2015 and 2020, the annual costs are predicted to go down to \$220 million and \$198 million, respectively.

Case	1	1 Ref	2	2 Ref	3	4	4 Ref	5	5 Ref
Storage and preparation	55	55	60	60	55	50	50	50	50
Pyrolysis	0	0	86	86	0	90	90	90	90
Gasification and cleaning	90	90	79	79	97	90	90	90	90
Gas conditioning	33	33	30	26	68	31	30	31	30
Fischer- Tropsch and conditioning	84	88	78	79	0	84	80	0	0
Lurgi Mt synfuel	0	0	0	0	96	0	0	84	81
Oxygen production	47	0	45	0	54	45	0	45	0
Power plant	24	0	21	0	28	23	0	23	0
Auxiliary plant infrastructure	81	43	131	90	110	89	57	89	56
Planning cost	74	60	90	71	82	71	57	71	57
Contingency	37	35	38	32	39	39	34	39	34
Total	525	398	658	523	629	612	488	612	488
Dry biomass input	700 000	700 000	700 000	700 000	700 000	700 000	700 000	700 000	700 000
Product output, hydrocarbons, t/yr	114 000	114 000	106 400	106 400	104 000	118 300	118 300	118 300	118 300

Table 3.7 Investment costs for different technology options in the DENA study

Note: Ref – integrated into refinery; option 3 not considered worthwhile integrating into a refinery. Source: Bridgewater (2009) and DENA (2006).

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## 3.4.3 Biofuel prices

Estimates of biofuel prices are given in Table 3.8. Although these are uncertain, several general points can be drawn from these estimates (The Royal Society, 2008):

- higher oil prices are beginning to make current biofuels commercially more attractive;
- cost reductions through economies of scale are expected for all biofuels, with lignocellulose technologies anticipated to be in the same range as food-crop technologies; and
- the post-tax prices of petrol and diesel fuels in Europe (less so in the USA) are often much higher than the pre-tax costs of biofuels; hence tax credits or other incentives, for example in the form of reductions in excise taxes on biofuels, would have a large effect on substitution.

However, these estimates do not take into account changes in prices and land values that may arise from competing demands from agriculture.

The economic prospects of biofuels will depend on improvements in yields both in the growth of the crops and in the efficiency of the conversion processes. Feedstock costs will also influence biofuel prices.

Biofuel	2006 (US cents/litre)	2030 (US cents/litre)
Price of oil (US\$/barrel)	50–80	
Corresponding pre-tax price of petroleum products (US\$/litre)	35–60	
Corresponding price of petroleum	150–200 in Europe	
products with taxes include, US cents/litre (retail price)	80 in USA	
Ethanol from sugar cane	25–50	25–35
Ethanol from corn	60–80	35–55
Ethanol from beet	60–80	40–60
Ethanol from wheat	70–95	45–65
Ethanol from lignocellulose	80–110	25–65
Biodiesel from animal fats	40–55	40–50
Biodiesel from vegetable oils	70–100	40–75
Fischer-Tropsch synthesis liquids	90–110	70–85

*Table 3.8* Estimated prices of biofuels compared with the prices of oil and oil products (biofuels exclusive of taxes)

Source: The Royal Society (2008).

### 3.5 Future trends

Future viability of biofuels will depend on a range of environmental, economic and social factors. Some of these include:

- land availability for the production of biofeedstocks;
- GHG emissions savings over fossil fuels, particularly when land-use change is involved;
- impact on biodiversity and water resources;
- feedstock and investment costs and the resulting biofuel prices;
- human health due to air pollution and human toxicity in the biofuels life cycle; and
- impact on food security.

In an attempt to ensure future sustainability of biofuels, an internationally accepted certification system has been proposed via the International Sustainability and Carbon Certification project (ISCC, 2009). The project aims to develop an international certification concept together with representatives from industry, trade, agriculture, policy makers and NGOs.

Initiative such as this as well as the growing international awareness and legislation related to biofuels may contribute towards more sustainable biofuels in the future.

# 3.6 Appendix: Life cycle assessment (LCA) methodology

Life cycle assessment (LCA) is an environmental management tool used for estimating the environmental burdens and impacts from a system – product, process or a service – over its whole life cycle. The life cycle stages normally included in LCA are extraction and refining of raw materials; product manufacture, distribution and use; disposal of wastes; and all transportation steps in between. The LCA methodology, as defined by the ISO 14040 and 14044 standards (ISO, 2006a, 2006b), is outlined in Fig 3.1A. It consists of four phases:

- Goal and scope definition;
- Life cycle inventory (LCI) analysis;
- Impact assessment (IA); and
- Interpretation.

*Goal and scope definition* is the first and most important phase of LCA. Here, the reasons for carrying out the LCA study as well as the intended audience are stated. The system boundary and the functional unit (unit of analysis) are defined as well as the impact assessment method to be used in the Impact assessment phase. Assumptions, limitations, cut-off rules, etc., are also described in this phase.

Life cycle inventory (LCI) analysis quantifies the environmental burdens in the system, i.e. materials and energy used and emissions discharged into the



3.1A The LCA methodological framework (ISO, 2006a).

environment. Allocation of environmental impacts is also carried out within LCI. Allocation is the process of assigning to each function of a multiple-function system only those environmental burdens that each functional output is responsible for. For example, if there are two or more co-products from a system, the environmental burdens should be allocated between them so as to reflect their contribution to those burdens. ISO 14044 (ISO, 2006b) recommends three methods for dealing with allocation:

- if possible, allocation should be avoided by disaggregating the given process into different sub-processes or by system expansion;
- if it is not possible to avoid allocation, then the allocation problem must be solved by using system modelling which reflects the underlying physical relationships among the functional units (e.g. mass or energy basis);
- where physical relationships cannot be established, other relationships, including economic value of the functional outputs, can be used.

The allocation method used will usually influence the results of the LCA study so that selection of an appropriate allocation method is crucial. Sensitivity analysis should be carried out in cases where the use of different allocation methods is possible to determine the influence of the allocation method on the results.

*Impact assessment* (IA) consists of several steps. First, categorisation of environmental impacts is carried out to determine which impacts will be considered.

Impact categories commonly considered in LCA are resource depletion, land use, global warming, acidification, ozone layer depletion, summer smog, eutrophication, human and eco-toxicity. This is followed by the characterisation step, to calculate the contribution of different burdens to the selected impact categories. The impacts are calculated by multiplying the 'potency factors' of each burden with its total life cycle emission. The potency factors indicate the potential of a burden to cause a particular impact and are expressed relative to a reference substance. For example, the potency factor for methane with respect to global warming is 25 kg CO<sub>2</sub> eq./kg CH<sub>4</sub>, indicating that methane is 25 times more potent global warming agent than CO<sub>2</sub>, whose potency factor is defined as unity.

The remaining two steps in IA – normalisation and valuation – are optional. The former normalises each impact to the total impact in a region or the world over a certain period of time, normally one year. In the valuation step, the impacts are aggregated into a single environmental impact index by assigning the weights of importance to the different impacts. This is the most subjective step in LCA and requires elicitation of preferences by stakeholders or decision makers.

*Interpretation* is the final LCA phase, whereby the results are interpreted depending on the goal of the study. This may include identification of the most significant impacts, 'hot spots' in the system and opportunities for improvements. Sensitivity analysis is also carried out within this phase.

Generally, there are two types of LCA studies: attributional and consequential (Curran *et al.*, 2001; Ekvall and Weidema, 2004). In attributional studies, the impacts are attributed to the system of interest (e.g. product) based on the flows in and out of the system as they are. For example in attributional LCA, impacts from the production of biofuel from wheat in the UK are estimated (attributed) based on the inputs and outputs from this system, not taking into account what happens with the other related activities in the economy, for example if the supply of wheat is constrained, e.g. due to its use for bread production. In consequential LCA studies, the aim is to estimate how the flows to and from the system would change as a result of different potential decisions. For example in the case of biofuels, a consequential LCA study would attempt to quantify the impacts of diverting wheat in the UK into biofuel production and having to supply food (e.g. bread) from alternative sources or from elsewhere in the world.

The attributional approach is used for labelling purposes (e.g. PAS2050 [BSI, 2008]) and certification systems (e.g. EU RED [EU, 2009]; Renewable Transport Fuel Obligation, RTFO [DfT, 2008]). Most biofuel LCA studies are also based on the attributional approach.

#### 3.7 Sources of further information

 $\mathrm{CO}_2$  tool for estimating GHG emissions from the production of transport fuels, electricity and heat from biomass

http://www.senternovem.nl/gave\_english/co2\_tool/index.asp

IEA Bioenergy

http://www.ieabioenergy-task38.org

Well-to-wheels evaluation of biofuels http://ies.jrc.ec.europa.eu/WTW

Biofuels sustainability scorecard http://idbdocs.iadb.org/wsdocs/getdocument.aspx?docnum=2152669

Biofuels and sustainability in Europe: http://www.biofuelstp.eu/sustainability.html

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**Abstract:** This chapter presents the most frequent vegetable-based feedstocks to biodiesel and bioethanol production. The chapter focuses on first- and second-generation biofuels with special emphasis on low-cost feedstocks. Finally, raw materials for developing technologies, including anaerobic digestion to produce biogas, Fischer-Tropsch from biomass, pyrolysis and biological production of bio-hydrogen are discussed.

**Key words:** first-generation biofuels, second-generation biofuels, third-generation biofuels, low-cost biofuels, biomass.

## 4.1 Introduction

Main differences between generations of biofuels lie in both conversion technology and raw materials. First-generation biofuels are made using conventional chemical technology to convert mainly oilseeds and grains into biodiesel and bioalcohol, respectively. In many cases, same feedstocks could be used for animal or human feeding purposes, thus suffering criticism from organisations that point at biofuels as the leading factor of food price rises and even deforestation in the Amazon or Indonesia. Although arguments against these assumptions are exposed, second-generation biofuels are based on non-food crops (i.e. Miscanthus) and biomass residues (from crops and forests), thus providing a socially accepted alternative. However, conversion technologies to produce biohydrogen, biodimethyether (Bio-DME), Fischer-Tropsch (FT) diesel, etc., are still under development.

There is also a third-generation emerging consisting of biofuels from algae and even an incipient fourth-generation based on the conversion of biodiesel into gasoline or on the recycling of carbon dioxide back into gasoline. Some companies claim that they can produce economically-sounded petroleum from microorganisms having the ability to efficiently convert renewable feedstocks into hydrocarbon-based fuels (Du, Li, *et al.*, 2008). Although there is a wide variety of feedstocks and biofuels, this chapter is mainly focused on the most frequent vegetable-origin feedstocks to biodiesel and bioethanol production.

# 4.2 Most frequent vegetable raw materials to produce first-generation biodiesel

## 4.2.1 Rapeseed/canola seed

Rapeseed (*Brassica napus*) is widely cultivated throughout the world for the production of animal feed, vegetable cooking oil and biodiesel (Fig. 4.1). The seeds contain about 40% oil, and after oil extraction, a rapeseed cake with 38–43% proteins remains. It belongs to the *Brassicaceae* family.

Rapeseed is one of the most important oilseeds in the world, ranking fourth with respect to production after soybean, palm and cottonseed (FAO/WHO/UNU, 2002). About 70% of the global production of biodiesel is based on rapeseed oil (Thoenes, 2006). Table 4.1 depicts oil yield from most common crops, whereas Table 4.2 presents the fatty acid composition of selected vegetable oils.



4.1 Brassica napus. (Photo courtesy of Shu Suehiro [http://www.botanic.jp/plants-sa/seabur.htm])

*Table 4.1* Oil yield from the most common oily crops used as feedstock for biodiesel production in 2007

Crop	Oil yield (kg/ha)	Oil yield (l/ha)
Corn ( <i>Zea mays</i> )	145	172
Soya ( <i>Glycine max</i> )	375	446
False flax (Camelina sativa)	490	n.a.
Ethiopian mustard (Brassica carinata)	n.a.	594
Sunflower (Helianthus annuus)	800	972
Castor (Ricinus communis)	1188	1413
Jatropha ( <i>Jatropha curcas</i> )	1590	1892
Palm ( <i>Elaeis guineensis</i> )	5000	5950

Source: Corre (2007).

	C12:0 wt.%	C14:0 wt.%	C16:0 wt.%	C16:1 wt.%	C18:0 wt.%	C18:1 wt.%	C18:2 wt.%	C18:3 wt.%	C20:1 wt.%	Others wt.%	Ref.
Asclepias syriaca oil			2–6	7	2–3	35	48	-		1	Holser (2003)
<i>Azadirachta indica</i> oil	I	I	18–23		17–25	40-43	15	Ι	1.3	Ι	Azam <i>et al.</i> (2005)
<i>Brassica carinata</i> oil	I	I	4-6		1–2	10–17	17–25	10–17	5-8	C22:1 (33–43); C24:1 (2)	Dorado <i>et al.</i> (2008); Dorado (2005)
Calophyllum inophyllum oil	I	I	18	1.5	16–18	40-45	13–14	2	I		Dorado <i>et al.</i> (2008); Hemavathy (1990)
<i>Camelina sativa</i> oil	I	I	5.5	I	2.5	13–17	12.5–18	36.5	1.5	C22:1 (15)	Dorado <i>et al.</i> (2008); Budin <i>et al.</i> (1995)
Castor oil	I	I	1–2	I	1–2	3-4	5–6	0.5	0.5	Ricinoleic (87–88)	Dorado <i>et al.</i> (2008); Meneghetti <i>et al.</i> (2006)
Cynara cardunculus oil	Ι		11	Ι	4	25	60		Ι		Dorado <i>et al.</i> (2008); Encinar, 1999
<i>Hevea brasiliensis</i> oil	I	I	10.2		8.7	24.6	39.6	16.3			Dorado <i>et al.</i> (2008); Ikwuagwu <i>et al.</i> , 2000
<i>Jatropha curcas</i> oil	I	I	14.35	0.8	6.4–6.6	36.5–41	35–42	0.3	I	I	Kumar and Sharma (2005, 2008); Berchmans and Hirata (2008)
<i>Mandhuca Indica</i> oil	I	-	16–24.2	I	20–22	41–43	9–14	I	ო	I	Dorado <i>et al.</i> (2008); Ghadge and Raheman (2005)
Olive oil			10–13	0.5–1	2–3	71–84	7–10	0.5-4	0.2	C20:0 (0.5)	Falk and Meyer-Pittroff (2004)
Palm oil	0.5	1–2	40–48	Ι	4–5	37–46	9–11	0.3	Ι	C 20:0 (0.3)	Rupilius and Ahmad (2007)
Peanut oil	I	I	8.2–15.1	I	1.1–7.2	55	25	0.2	0.8–3	C22:0 (1.8–5.4)	Kaya <i>et al.</i> (2009); Aydin (2007); Ozcan and Seven (2003)
<i>Pongamia pinnata</i> oil	I	I	3.7–7.9	I	2.4-8.9	64.5–71.3	10.8– 18.3	I	I	C24:0 (1–3.5)	Meher <i>et al.</i> (2004); Azam <i>et al.</i> (2005); Naik <i>et al.</i> (2008)
Rapeseed oil	I	I	3–5	I	1–2	55–65	20–26	8-10	1-2	C 22:0 (0.5)	Komers <i>et al.</i> (2001); Jeong <i>et al.</i> (2004)
Soybean oil			11–12	Ι	3–5	23–25	52–56	6–8			Freedman <i>et al.</i> (1986)
Sunflower oil	I		6	I	3–5	17–22	67–74		I	C22:0 (0.6)	Vicente <i>et al.</i> (1998)
<i>Terminalia catappa</i> oil			35		5	32	28	I		I	Abdullah and Anelli (1980)

Several studies have investigated the optimisation and kinetics of alkalicatalysed transesterification reaction for the production of biodiesel from rapeseed oil (Komers *et al.*, 2001; Jeong *et al.*, 2004; Rashid and Anwar, 2008). To avoid drawbacks due to the use of catalysts, supercritical ethanol and methanol as reagents have also been researched (Kusdiana and Saka, 2001; Saka and Kusdiana, 2001; Warabi *et al.*, 2004; Wang *et al.*, 2007; Balat, 2008; Lim *et al.*, 2009). Jeong and Park (Jeong and Park, 2008) evaluated the efficacy of a transesterification process for rapeseed oil with methanol in the presence of an enzyme and tertbutanol, which was added to ameliorate the negative effects associated with excess methanol. The inclusion of auxiliary energies as microwave heating to improve the conversion to biodiesel has also been studied (Azcan and Danisman, 2008).

Canola, which derives its name from Canadian oil with low erucic acid, is a rapeseed cultivar (*Brassica napus* L. and *B. campestris* L.). The main use of the oilseeds is human consumption due to the lower level of erucic acid compared to traditional rapeseed oils. It is also used to produce livestock feed due to reduced levels of the toxin glucosinolates in the cake.

Dubé *et al.* (2007) developed a two-phase membrane reactor to produce biodiesel from canola oil and methanol using both acid- and base catalysis, under different temperatures. The novel two-phase membrane reactor was particularly useful in removing unreacted canola oil from the fatty acid methyl ester product yielding a high purity biodiesel. Further studies with membranes reactors of varying pore sizes have shown that canola oil was retained in the reactor, which indicated that the oil droplets were larger than the tested pore sizes (Cao *et al.*, 2009).

In the last decades, several engine tests have been carried out to study the performance and emissions of rapeseed/canola oil methyl ester (ROME) in diesel engines. Straight and blended biodiesel (with diesel fuel) have been tested showing an increase in break-specific fuel consumption (BSFC) up to 14% and 3%, respectively (Hansen and Jensen, 1997; Turrio-Baldassarri *et al.*, 2004; Ozsezen *et al.*, 2009). The increase in BSFC with biodiesel seems to be proportionally related to the decrease of lower heating value (Senatore *et al.*, 2000; Tsolakis, 2006). However, Romig and Spataru (1996) tested six different biodiesel blends and found no differences in engine performance compared to diesel fuel. Kegl (2008) found that the high mean injection pressure and mean injection rate of straight biodiesel offer a potential to reduce harmful smoke and NO<sub>x</sub> emission. By retarding the injection timing from 23° to 19°CA BTDC, other harmful engine emissions were also reduced (CO, HC).

#### Green canola seed

Green seed canola oil is a low-quality green oil. This particular colour is due to the high chlorophyll content that is retained in the mature canola seeds due to exposure to sublethal frost  $(0-5^{\circ}C)$  during seed development (Johnson-Flanagan

*et al.*, 1990). Compared to green seed canola oil, pure canola oil has a crystal yellow colour with low chlorophyll content and is produced from canola seeds with low green seed content.

The cost of processing green seed canola oil for edible purposes is high. Oil with high chlorophyll content cannot be used for manufacture of margarine since chlorophyll can inhibit the activity of hydrogenation catalyst (Abraham and de Man, 1986). Also, this oil cannot be used for edible purposes because the high chlorophyll content seriously affects the stability of the oil, causing rapid formation of oxidation products via the photosensitised singlet oxygen pathway (Rawls and Van Santen, 1970). The oxidative degradation of oil produces a number of volatile products that provide a bad odour to the oil. To remove chlorophyll, bleaching can be used; however, this can have a deleterious effect on the stability of a vegetable oil (Tautorus and Low, 1994). Processing conditions used for bleaching could produce new compounds from chlorophyll derivatives in the crude oil. Thus, green seeds are not recommended for feeding purposes. The percentage of green seeds is one of the major gradation factors for canola seeds.

However, tests to produce biodiesel from green seeds oils have been successfully performed. Kulkarni *et al.* (2006) found that the cloud point of green seed esters is lower than that of pure canola oil esters due to higher content of linoleic and linolenic acids. Furthermore, green seed esters have also been proposed as additive and the use of 1% (v/v) added to ultra-low sulphur diesel fuel to reduce the wear scar area and increase the lubricity has been recommended. Oxidation stability of methyl ester obtained from green seed canola oil is lower (4.9 hours at 110°C) than the European Standard EN 14214. Biodiesel originating from green seed canola oil shows good fuel quality parameters, but its oxidative stability needs to be improved to be considered a viable diesel fuel alternative (Kulkarni *et al.*, 2006).

#### 4.2.2 Sunflower seed

Sunflower (*Helianthus annuus L.*), a member of the *Compositea* family, is an important oilseed crop worldwide (Fig. 4.2), yielding approximately 45–50% oil and the quality depending on the region (Pereyra-Irujo *et al.*, 2009). The feasibility of sunflower oil used as a raw material for biodiesel production has been extensively researched in Spain, including homogeneous and heterogeneous catalysts (Vicente *et al.*, 1998, 2004, 2005; Antolín *et al.*, 2002; Arzamendi *et al.*, 2006, 2008; Ramos *et al.*, 2008). Auxiliary energies, such as low frequency ultrasonication, have been proposed to enhance the reaction yield in transesterification reactions using ethanol (Georgogianni *et al.*, 2008).

Diesel engine tests have also been performed showing a power loss up to 10% when the engine was run on biodiesel (Kaplan *et al.*, 2006). However, the use of blends with diesel fuel up to 30% biodiesel reported no significant changes in BSFC (Neto da Silva *et al.*, 2003).  $CO_2$ , CO and  $NO_x$  emissions seem to be lower than those of diesel fuel (Ilkilic, 2008). The use of straight sunflower oil in



*4.2 Heliantus annus.* (Photo courtesy of Fabio Visentin [http://www. fabiovisentin.com])

an indirect injection diesel engine also exhibits exhaust emissions reduction and no negative effects on the engine performance (Canakci *et al.*, 2009).

## 4.2.3 Palm kernel

*Elaeis guineensis* is an edible oleaginous plant known as palm. The rapid increase in the production in the last 20 years has made palm oil the most important oil in the world. It is preferred for its high productivity, which explains its rapid expansion (Rupilius and Ahmad, 2007). Palm kernel oil is extremely important for the oleochemical industry because of the fatty acids profile (Ahmad, 2006). In the past decade, some researchers also found the feasibility of palm oil to produce biodiesel using either homogeneous (Darnoko and Cheryan, 2000; Crabbe *et al.*, 2001) or heterogeneous catalysts (Jitputti *et al.*, 2006).

Comparing the use of diesel fuel to run diesel engines, pure biodiesel exhibits an increase in BSFC up to 17% (Lin *et al.*, 2006), while mixtures of 20% biodiesel with diesel fuel showed a lower increase of 3.3%. Altitude can play an important role, as better engine performance is achieved at high altitudes due to the influence in the duration of the premixed combustion stage (Benjumea *et al.*, 2009). Even biodiesel from waste palm oil causes reductions in CO, HC and smoke opacity, while NO<sub>x</sub> increases (Ozsezen *et al.*, 2009). The use of additives in 20% biodiesel blends seems to improve the previous results (Kalam and Masjuki, 2008). This oil has also been used straight and preheated, showing no negative effects on the engine, although exhaust emissions increased (Bari *et al.*, 2002). The use of pure oil blended in low percentages with diesel fuel showed no signs of engine deterioration, while engine performance was not affected (Sapaun *et al.*, 1996).

## 4.2.4 Soybean seed

Soybean (*Glycine max* Merr.) oil is used as both edible oil and transportation fuel (Fig. 4.3). However, oxidative instability and cold flow in northern climates have



4.3 Glycine max. (Photo courtesy of Huw Williams)

limited usefulness of a soybean oil-derived biodiesel. Implementing the tools of biotechnology to modify the fatty acid profile of soybean for locale performance enhancement may increase the attractiveness of biodiesel derived from this commodity crop (Kinney and Clemente, 2005).

More than 20 years ago, researchers demonstrated the feasibility of the production of biodiesel from soybean oil using methanol in the presence of homogeneous catalysts (Freedman *et al.*, 1986). Since then, research has been conducted under supercritical and subcritical methanol (Wang and Yang, 2007) and with heterogeneous catalysts (Xie and Huang, 2006; Liang *et al.*, 2009). Diesel engines have been run on soybean oil biodiesel, straight or 20% blended with diesel fuel, showing an increase in BSFC up to 18% and 2.5% respectively, compared to the use of diesel fuel. It has been found that the oil origin has no influence over BSFC (Canakci and Van Gerpen, 2001; Hess *et al.*, 2007). Furthermore, in the 1950s, 20% waste soybean oil blended with 80% diesel fuel was successfully used to run the University bus at Ohio State University (Fishinger, 1980).

### 4.2.5 Peanut seed

Peanut is an annual crop grown predominantly in the Mediterranean region (Aydin, 2007). *Arachis hypogaea* L., of the *Fabaceae* family, develops in an underground pod containing two seeds (Fig. 4.4). It is widely cultivated in warm climates and has short yellow flowers. Most peanuts grown in the world



4.4 Arachis hypogaea. (Photo courtesy of José María Fernández)

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are used for oil production, peanut butter, confections and snack products (Yu *et al.*, 2007). Peanut oil is a pale yellow oil with a distinctive nutty taste and odour obtained from the processing of peanut kernel (Oyinlola *et al.*, 2004; Aydin, 2007).

Studies about biodiesel production from peanut oil have been carried (Kaya *et al.*, 2009) out and minimisation of the concentration of long-chain saturated fatty acids has been suggested, either through processing or breeding efforts, to improve cold weather properties (Davis *et al.*, 2009). Even Rudolf Diesel (1900) used straight peanut oil to run the diesel engine. In 1911, he wrote 'The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of countries which will use it' (Kaya *et al.*, 2009).

## 4.3 Raw materials to produce low-cost biodiesel

In temperate areas, annual oilseeds such as soybean, canola and sunflower have been largely used as biodiesel feedstocks, while palm oil trees have been used as feedstock in the tropics. However, the use of non-edible, low-input, low-cost and sustainable vegetable feedstocks compatible with good quality biodiesel (to achieve both customer and vehicles manufacture trust) should be the scientific community target. According to the previous requirements, the following section presents the most suitable vegetable raw materials for biodiesel production. The selection has been prepared considering low input and most promising crops according to their fuel properties (Dorado, 2008). Oleaginous crops to produce biodiesel, such as Bahapilu, castor, cotton seed, cuphea, *Jatropha curcas*, karanja seed, linseed, mahua, nagchampa, neem, rubber seed, tonka bean; low-cost edible oils, such as cardoon, Ethiopian mustard, Gold-of-pleasure, tigernut; and potential oil-bearing crops and trees such as allanblackia, bitter almond, chaulmoogra, papaya, sal, tung and ucuuba have already been revised by the authors and an extensive revision can be found in a previous work (Dorado, 2008).

### 4.3.1 Asclepias syriaca seed

This common milkweed (Fig. 4.5) is native from the Northeast and North Central United States where it grows on roadsides and in undisturbed habitat (Holser, 2003). On the basis of the fatty acid profile, the oil is expected to provide an alternative source to biodiesel production (Adams *et al.*, 1984). Milkweed oil contains more than 6% of palmitoleic acid that is a strong candidate to enhance fuel properties, besides methyl oleate (Knothe, 2008).

Engine performance tests using biodiesel have been analysed by few authors that found appropriate cold weather properties (Holser and Harry-O'Kuru, 2006). Highly unsaturated ester structures oxidise more rapidly than the saturated ones. These oxidative processes lead to degradation of the fuel and reduce its quality.

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4.5 Asclepsia syriaca. (Photo courtesy of Moreno Clementi)

## 4.3.2 Moringa oleifera seed

The Moringaceae is a single-genus family of oilseed trees with 14 known species. Of these, the fast growing, drought-tolerant *Moringa oleifera*, which ranges in height from 5 to 10 m, is the most widely known and utilised (Morton, 1991). *M. oleifera* thrives best in a tropical insular climate and is plentiful near the sandy beds of rivers and streams. *M. oleifera* can tolerate wide rainfall range (25–300 cm per year) and soil pH from 5.0 to 9.0 (Rashid *et al.*, 2008). *M. oleifera* seeds contain between 33% and 41% w/w of vegetable oil (Somali *et al.*, 1984; Anwar and Bhanger, 2003; Anwar *et al.*, 2005) and are rich in oleic acid (> 70%). *M.* 

*oleifera* is commercially known as 'ben oil' or 'behen oil', due to its content of behenic (docosanoic) acid, and possesses significant resistance to oxidative degradation (Lalas and Tsaknis, 2002).

*M. oleifera* has many medicinal uses and significant nutritional value (Anwar, 2007). A survey conducted on 75 indigenous (Indian) plant-derived non-traditional oils concluded that *M. oleifera* oil has a good potential for biodiesel production (Azam *et al.*, 2005). Acid pretreatment is needed to reduce the acid value, but the resulting biodiesel exhibits one of the highest cetane number (around 67) found for biodiesel (Rashid *et al.*, 2008).

## 4.3.3 Terminalia catappa

*Terminalia catappa* is popularly known in Brazil as 'castanhola' (dos Santos *et al.*, 2008). The tree is tolerant to strong winds and moderately high salinity in the root zone (Fig. 4.6). It grows principally in freely drained, well-aerated and sandy soils.

The oil is obtained from the kernels of the fruit (that is non-edible and considered a waste), with yields around 49% w/w (Abdullah and Anelli, 1980). Biodiesel production, using either basic or acid catalysts, has been studied, concluding that basic catalysts performed more efficiently producing a yield of ca. 93% biodiesel (dos Santos *et al.*, 2008).

## 4.4 Vegetable raw materials to produce bioethanol

Ethanol (i.e. ethyl alcohol, bioethanol) is a liquid oxygenated biofuel employed either as a fuel or as an additive. When it is used as the latter, due to its high oxygen content, a less amount of additive is required. The increased percentage of oxygen allows a better oxidation of the gasoline hydrocarbons with the consequent reduction in the emissions of CO and aromatic compounds (Sanchez and Cardona, 2008).

Bioethanol is the most widely used biofuel for transportation applications, specially in the Western hemisphere, where it surpasses biodiesel in importance. One major problem related to bioethanol production is the availability of the raw materials that varies considerably from season to season and depends on geographic location (UNCTAD, 2006). The major global producer of bioethanol is Brazil, which produces 50% of the world fuel ethanol, using sugar cane juice (Brazil is responsible for 25% of all sugar cane production worldwide) and molasses (Murphy, 2004). In the USA, 95% of the fuel ethanol produced comes from corn, while more temperate countries like Canada uses other less efficient starchy crops like wheat, corn and barley (Murphy, 2004). Table 4.3 depicts ethanol yield from the most common crops.

Biological feedstocks that contain appreciable amounts of sugar – or materials that can be converted into sugar, such as starch or cellulose – can be fermented to produce bioethanol (Kim and Dale, 2004). Bioethanol feedstocks can be classified

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4.6 Terminalia catappa. (Photo courtesy of Bruno Navez)

Table 4.3 Bioethanol	yield from	different	feedstocks	in 2007
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Feedstock	Bioethanol (hl/t of feedstock)
Sugar beet	1
Molasses	3
Wheat	3.6

Source: Corre (2007).

into three types: (1) sucrose-containing feedstocks (e.g. sugar beet, sweet sorghum and sugar cane); (2) starchy materials (e.g. wheat, corn and barley); (3) lignocellulosic biomass (e.g. wood, straw and grasses).

The price of the raw materials can highly affect the production costs of bioethanol because feedstocks typically account for more than one-third of the production costs, and maximising bioethanol yield is imperative (Murphy, 2004). In this sense, sugar cane and sugar beet present an alcohol yield of around 3 and 1 hl/t respectively, while cereals such as wheat and corn present higher alcohol yields (3.6 and 4 hl/t, respectively). However, processing costs to produce ethanol from sugar cane and sugar beet (where sugars are easily accessible since disaccharide can be broken down by the yeast cells) are lower compared to cereals and most of all compared to starchy materials and lignocellulosic biomass (Cardona and Sánchez, 2007; Prasad *et al.*, 2007). Starchy, lignocellulosic, urban and industrial wastes need costly pretreatment to convert into fermentable substrates.

## 4.4.1 Sucrose-containing feedstocks

The main feedstock for ethanol production is sugar from cane and beet. Sugar is converted into bioethanol by ethanologenic fermentation. The most employed microorganism is *Saccharomyces cerevisiae* due to its capability to hydrolyse cane sucrose into glucose and fructose, two easily assimilable hexoses (Sanchez and Cardona, 2008). Yeasts such as *Schizosaccharomyces pombe* present the additional advantage of tolerating high osmotic pressures (high amounts of salts) and high solids content (Bullock, 2002). Among bacteria, *Zymomonas mobilis* provides higher ethanol yield, up to 97% of theoretical maximum (Claassen *et al.*, 1999). The disadvantage of its use during fermentation is the formation of a polysaccharide (which increases the viscosity of fermentation broth) and sorbitol, which decreases the efficiency of the conversion of sucrose into ethanol (Lee and Huang, 2000).

#### Sugar cane and sugar beet

Feedstock for bioethanol production is essentially composed of sugar cane (Fig. 4.7) or molasses (by-product of sugar mills) and sugar beet (Fig. 4.8) (UNCTAD, 2006). Two-third of the world sugar production is from sugar cane and one-third is from sugar beet. Sugar cane is grown in tropical and subtropical countries, while sugar beet is only grown in temperate climate countries.

While Brazil is the world's largest producer, in European countries, Spain is the largest producer of bioethanol, and beet molasses are the most utilised sucrosecontaining feedstock (Cardona and Sánchez, 2007). Sugar beet crops are grown in most of the European Union (EU) member states, providing 90% of the total EU demand of sugar. The advantages of sugar beet are a lower cycle of crop

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4.7 Sugar cane. (Photo courtesy of Hannes Grobe)



4.8 Sugar beet. (Photo courtesy of Biofuels Center of North Carolina [http://www.biofuelscenter.org])

production, higher yield and high tolerance of a wide range of climatic variations, low water and fertiliser requirement. Compared to sugar cane, sugar beet requires 35–40% less water and fertiliser (Balat *et al.*, 2008).

#### Sorghum bicolor

*Sorghum bicolor* crop, also known as sweet sorghum (Fig. 4.9), is heat tolerant and is one of the most drought-resistant crops as it has the capability to remain dormant



4.9 Sorghum bicolor. (Photo courtesy of Daniel Georg Döhne)

during the driest periods, so it can grow in marginal land (Yuan *et al.*, 2008). Sweet sorghum is one of the most promising candidates for bioethanol production in developing countries because it produces grains with high starch content, stalks with high sucrose content and leaves and bagasse with high lignocellulosic content (Smith and Buxton, 1993). It has been found that the production of ethanol from the hemicellulose and cellulose in bagasse is more favourable than burning it to make power in North China, although ethanol produced from the juice is very sensitive to the price of sugar (Gnansounou *et al.*, 2005).

## 4.4.2 Starchy materials

Starch is a biopolymer, defined as a homopolymer, consisting of only one monomer, D-glucose (Pongsawatmanit et al., 2007). To produce bioethanol from starch, it is necessary to break down by hydrolysis the chains of this carbohydrate to glucose syrup or fermentable sugar that can be converted into bioethanol by yeasts (Balat et al., 2008). This type of feedstock, mainly corn and wheat, is the most utilised for bioethanol production. The starch-based bioethanol industry has been commercially viable for about 30 years (Barretts de Menezes, 1982). In that time, tremendous improvements have been made in enzyme efficiency, reducing process costs and time and increasing bioethanol yields (Kim and Dale, 2004). However, there are two main reasons for the present high cost: on the one hand, the usual yeast S. cerevisiae cannot utilise starchy materials, so large amounts of amylolytic enzymes, namely glucoamylase and  $\alpha$ -amylase, need to be added (Apar and Özbek, 2004); on the other hand, the starchy materials need to be cooked at a high temperature (413–453 K) to obtain a high bioethanol yield. In the last years, the possibility of hydrolysing starch at low temperatures (liquefaction) for achieving energy savings has been investigated (Shigechi et al., 2004; Mojovic et al., 2006; Robertson et al., 2006).

#### Zea mays

Ethanol is produced almost exclusively from corn in the USA. Corn is milled for extracting starch that is enzymatically treated for obtaining glucose syrup. Then, this syrup is fermented into ethanol. There are two types of corn milling in the industry: wet and dry. During wet milling process, corn grain is separated into its components.

Fermentation may be performed using *S. cerevisiae* at  $30-32^{\circ}$ C with the addition of ammonium sulfate or urea as nitrogen sources (Sanchez and Cardona, 2008). Proteases can be added to the mash to provide an additional nitrogen source (Bothast and Schlicher, 2005). *Z. mobilis* has also been researched for ethanol production from dry-milled corn starch (Krishnan *et al.*, 2000). Other research efforts are oriented to the development of corn hybrids with higher extractable or fermentable starch content (Bothast and Schlicher, 2005).

#### Triticum spp.

Ethanol is produced from wheat (Fig. 4.10) by a process similar to that of corn. Some efforts have been done for optimising fermentation conditions (Thomas *et al.*, 1996; Wang *et al.*, 1999; Bayrock and Michael Ingledew, 2001; Barber *et al.*, 2002; Soni *et al.*, 2003). Cost is the main drawback of this alternative.

The bran fraction, which would normally be a waste product of the wheat milling industry, can be used as the sole medium to produce enzyme complexes (Dorado *et al.*, 2009). The proposed process could be potentially integrated into a wheat milling process to upgrade the wheat flour milling by-products into platform chemicals of a sustainable chemical industry (Du, Lin, *et al.*, 2008). If the production of co-products is optimised and residues are integrated into the process, ethanol from wheat may become a serious competitor of gasoline as a fuel.

#### Manihot esculenta

*Manihot esculenta*, a perennial woody shrub with an edible root used in feed formulations, is also known as cassava and tapioca (Fig. 4.11). It grows in many parts of tropical and subtropical areas, specially in places where the soil is relatively poor and other crop yields are low (Mojovic *et al.*, 2006).

Ethanol production from cassava can be accomplished using either the whole cassava tuber or the starch extracted from it (López-Ulibarri and Hall, 1997; Zhang *et al.*, 2003). Starch extraction can be carried out through a high-yield, large-volume



4.10 Tritucum aestivum. (Photo courtesy of Hans Hillerwaer)



*4.11 Manihot esculenta.* (Photo courtesy of Botanische tuin TU Delft in Delft, The Netherlands)

industrialised process such as the Alfa Laval extraction method (FAO, 2004) or by a traditional process for small- and mid-scale plants. This process can be considered as the equivalent of the wet milling process for ethanol production from corn, while fuel ethanol production from whole cassava is equivalent to ethanol production from corn by dry milling technology. Due to its high moisture content, cassava should be transported as soon as possible from cropping areas considering its rapid deterioration (Sanchez and Cardona, 2008). Authors have found that to make ethanol competitive to gasoline, the combination of increasing crop yield and decreasing farming costs is required (Nguyen *et al.*, 2008).

# 4.4.3 Lignocellulosic biomass

Lignocellulosic biomass, including agricultural residues, wood and energy crops, is an attractive material for bioethanol production. Lignocellulosic biomass could produce up to 442 billion litres per year of bioethanol (Bohlmann, 2006), which is about 16 times higher than the current world bioethanol production (Kim and Dale, 2004). Furthermore, about 3.6% of the world's electricity production and  $2.6 \times 10^{12}$  MJ of steam are also generated from burning lignin-rich fermentation residues, a co-product of bioethanol made from crop residues and sugar cane bagasse. Most potential electricity and steam production could be provided by burning fermentation residues in the utilisation of wheat straw (Sun and Cheng, 2002).

Conversion of cellulosic biomass is a future alternative of biofuel production. However, bioconversion of cellulosics and lignocellulosics to bioethanol is difficult due to the resistant nature of biomass to breakdown, the variety of sugars that are released when the hemicellulose and cellulose polymers are broken, the need to find or genetically engineer organisms to efficiently ferment these sugars and costs for collection and storage of low density lignocellulosic feedstocks (Balat *et al.*, 2008). Provided that cellulases and pretreatment processes are expensive, genetically modified crops to reduce the needs for pretreatment processes are promising paths to solve this problem, together with other strategies, such as increasing plant polysaccharide content and overall biomass (Sticklen, 2008).

Forest and agricultural residues may be used to produce bioethanol. As an advantage, there would not be a strong competition between the use of land for food and for energy. Sorghum seeds can be used for food, while the stems could be optimised for different chemical platforms. Recent studies concluded that sweet sorghum is a very useful plant, whereby the complete plant can be used without leaving any waste (Smith and Buxton, 1993; DSD, 2005). Lignocellulosic biomass of cardoon can be used as a solid biofuel, while seed oil can be derived for biodiesel production (Fernández *et al.*, 2006). Lately, the production of ethanol fuel from cardoon stems and leaves has been proposed (Martinez *et al.*, 1990).

New crops that have been evaluated as bioenergy crops over the last years include switchgrass and elephant grass. Provided they cannot be used for feeding purposes, they seem to successfully substitute cereals, such as corn, to produce bioenergy. Lignocellulosic perennial crops (e.g. short rotation coppices and inedible grasses), especially warm-season (plants with  $C_4$  carbon fixation) perennial grasses, are promising feedstocks because of high yields, low costs, good suitability for low quality land (which is more easily available for energy crops) and low environmental impacts (Cherney *et al.*, 1991).

Another group of dedicated bioenergy feedstocks is woody plants, including hybrid poplar, willow and pines. Hybrid poplar is considered a model woody biomass feedstock because of its broad adaptation, available genome sequence and fast growth. The biomass accumulation of hybrid poplar is reported to be between 7 and 20 mg/ha/year depending on the nutrition and environmental conditions (Christersson, 2006; Yuan *et al.*, 2008).

#### Rice straw

Rice straw is one of the more abundant lignocellulosic waste materials in the world (Fig. 4.12), reaching 731 million tons per year. This amount of rice straw can potentially produce 205 billion litres bioethanol per year, which would be the largest amount from a single biomass feedstock (Bohlmann, 2006). By selecting high-biomass yielding species, combined with high nutrient and water use efficiency, economically efficient production of biofuel feedstock may be realised on less optimal land without pressuring prime grain crop territories (Jakob *et al.*, 2009).



4.12 Rice straw. (Photo courtesy of Brad Lashua)

#### Panicum virgatum

*Panicum virgatum*, also known as switchgrass (Fig. 4.13), is a native perennial warm-season ( $C_4$  plant) grass with deep roots, growing on relatively poor quality lands, where water and nutrient availability would prevent the successful production of conventional crops. A widely adapted endemic species, it is an important ecological component of North American native grassland ecosystems (Lewandowski *et al.*, 2003).

One of the advantages of switchgrass is that it can be harvested and handled with conventional hay-making equipment (Cundiff and Marsh, 1996; Sokhansanj *et al.*, 2009). Switchgrass combines more of the attributes desirable for bioenergy feedstock production than other grasses. These attributes include distribution and high productivity across a wide geographical range and on diverse agricultural sites, high water use and nutrient use efficiency, and positive environmental attributes – including effects on soil quality and stability, cover value for wildlife and relatively low inputs of energy, water and agrochemicals required per unit of energy produced (McLaughlin and Walsh, 1998). Comparing corn and switchgrass on marginal soils for biofuel production, Varvel *et al.* (2008) found that the potential ethanol yield from switchgrass was equal to or greater than the potential total ethanol yield from corn grain.

#### Miscanthus giganteus

*Miscanthus giganteus* is a tall (up to 3 m) perennial sterile grass originating from Japan (Hodkinson *et al.*, 2002). It can be harvested yearly with a sugar cane



*4.13 Panicum virgatum.* (Photo courtesy of Rich Weber in Native Trees of Indiana website)

harvester and can be grown under cool climates like that of northern Europe and USA. Like other bioenergy crops, stems may be burned for heat and electric power production or fermented to ethanol. It combines many of the desirable properties of a biofuel crop. As a perennial  $C_4$  plant, it produces consistently high biomass yields (8–15 tons/ha dry weight) over many years with little or no nitrogen application, shows good energy balance and low mineral content, which improves fuel quality. However, the yield potential might not be fully used when this variety is cultivated under varying climatic conditions. Interspecific crosses between sorghum and *Miscanthus* could complement *Miscanthus* in adaptation to stress conditions in arid climates. Similarly, Miscane, a hybrid between sugar cane and *Miscanthus*, could potentially combine the high productivity of both species with the perenniality and adaptation of *Miscanthus* to colder climates (Jakob *et al.*, 2009).

#### Pennisetum purpureum

*Pennisetum purpureum*, also known as elephant grass (Fig. 4.14), is a species of grass native to the tropical grasslands of Africa. It is a tall (2–4.5 m) perennial plant with a very high productivity, both as a forage grass for livestock and as a biofuel crop. It is usually harvested before winter, so it can be burnt in power plants (Langeland *et al.*, 2008).

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4.14 Pennisetum purpureum. (Photo courtesy of Mehmet Karatay)

#### Helianthus tuberosus

*Helianthus tuberosus*, also called Jerusalem artichoke, sunroot, sunchoke, earth apple and topinambur, is a species of sunflower native to the eastern United States that can grow up to 3 m high (Fig. 4.15). Due to its high alcohol yield (5000–6000 l/ha in Spain), Jerusalem artichoke also has an unused great potential as a producer of ethanol fuel from stems. Tubers are an important source of fructose for industry (Huxley *et al.*, 1992; Davidson *et al.*, 2006).

# 4.5 Vegetable raw materials to produce biofuels from other technologies

### 4.5.1 Biomass

Biomass is a promising feedstock for anaerobic digestion. Grasses, including straws from wheat, rice and sorghum, are a plentiful supply of biomass, most of which is a waste product from food industry. Methane yield values are typically high, although the high proportion of recalcitrant materials often requires pretreatments to fulfil the potential yield (Lissens, Thomsen, *et al.*, 2004; Lissens, Verstraete, *et al.*, 2004; Petersson *et al.*, 2007). Harvesting time can also significantly affect the biogas yield of plants. As an example, maize produces ca. 40% greater methane yields at 97 days of vegetation when compared to 151 days of vegetation (Amon *et al.*, 2007).



4.15 Helianthus tuberosus. (Photo courtesy of Paul Fenwick)

#### Biomass for the Fischer-Tropsch synthesis

In an FT complex, the production of purified syngas typically accounts for 60–70% of the capital and running costs of the total plant (Dry, 2002). The most popular feedstock to provide syngas for the FT synthesis has been coal (German vehicles during the Second World War), but nowadays, natural gas is gaining in importance. Sources of gas are either large, remote reserves of natural gas or the so-called associated gas that cannot be flared any more due to more severe  $CO_2$  emission regulations (Dry, 2002; Prins *et al.*, 2005).

Biomass has not yet been commercially applied as a feedstock for the Fischer-Tropsch synthesis (FTS); however, the integration of biomass gasification with FTS has been demonstrated (Boerrigter and den Uil, 2002). Prins *et al.* (2005) carried out an exergy analysis of biomass integrated gasification FTS, and the maximum thermodynamic efficiency achieved was 46.2%, consisting of 41.8% fuels and 4.4% electricity. The thermodynamic analysis showed that a mild thermal pretreatment of the biomass may improve gasification properties, that is heating value and moisture content. Although proof-of-concept of straw gasification technology scalable to an on-farm production has been demonstrated, little is known about differences among grasses in their suitability as gasification feedstock (Prins *et al.*, 2005).

## 4.5.2 Fruit and vegetable wastes

Fruit and vegetable wastes present low total solids and high volatile solids and are easily degraded in anaerobic digesters. The rapid hydrolysis of these feedstocks may lead to acidification of the digester and the consequent inhibition of methanogenesis. Many carbohydrate-rich feedstocks require either co-digestion with other feedstocks or addition of alkaline buffer to ensure stable performance (Wieger *et al.*, 1978). A solution may be provided by two-stage reactors that use the first stage as a buffer against the high organic loading rate, which offers some protection to the methanogens. Separation of the acidification process from methanogenesis by the use of sequencing batch reactors has shown to give high stability, a significant increase in biogas production and an improvement in the effluent quality when used with fruit and vegetable waste (Bouallagui *et al.*, 2004).

# 4.5.3 Feedstock used for pyrolysis (thermal cracking) and bio-hydrogen production

Pyrolysis refers to material chemical change caused by the application of thermal energy in the presence of air or nitrogen (Fukuda *et al.*, 2001). The pyrolysis of different triglycerides was used for fuel supply in different countries during the First and Second World Wars. For instance, a tung oil pyrolysis batch system was used in China as a hydrocarbon supply during the Second World War (Lima *et al.*, 2004).

Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil (Lima *et al.*, 2004). Many kinds of vegetable oil species have been subjected to pyrolysis conditions. Some of these vegetable oils are soybean (da Rocha Filho *et al.*, 1993; Lima *et al.*, 2004), rapeseed (Billaud *et al.*, 1995), palm tree (Alencar *et al.*, 2002; Lima *et al.*, 2004,), castor (Lima *et al.*, 2004), safflower (Billaud *et al.*, 1995), olive husk (Demirbas *et al.*, 2000) and tung (Chand and Wan, 1947). Soybean oil pyrolysed distillate, which consists mainly of alkanes, alkenes and carboxylic acids, has a cetane number of 43,

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exceeding that of soybean oil (37.9) and the ASTM (American Society for Testing and Materials) minimum value of 40. The viscosity of the distillate was higher than the ASTM specification for diesel fuel but considerably below that of soybean oil (Lima *et al.*, 2004). Short-term engine tests have been successfully carried out on this fuel (Hu *et al.*, 2000). Used frying cottonseed oil pyrolysate has also been investigated (Knothe *et al.*, 1997).

Biological production of hydrogen (bio-hydrogen) has received special attention during the last decade because it can be operated at an ambient temperature and pressure and is more environmentally friendly compared to other processes (Mohan *et al.*, 2007). Due to the low cost and regeneration properties, biotechnology of hydrogen production might be the most important way for energy production in the near future (Balat and Balat, 2009). Furthermore, it offers sustainable supply of hydrogen with low pollution and high efficiency from a variety of renewable resources (Cheong and Hansen, 2006; Wu and Chang, 2007). Biological hydrogen production can be classified into the following groups:

- 1 Direct biophotolysis: The process uses the photosynthetic capability of green algae and cyanobacteria to split water by the directly absorbed light energy and concomitant transfer of electrons to a hydrogenase or a nitrogenase for  $H_2$  production (Kovács *et al.*, 2006).
- 2 Indirect biophotolysis: This process involves a photosynthetic biomass production step and an anaerobic dark fermentation of the biomass to produce  $H_2$ . Several models to achieve indirect biophotolysis have been developed. These systems use algae in most cases and intend to exploit their capability to produce high biomass yield per surface. Main research includes production of algal biomass, which is rich in easily fermentable storage carbohydrates (Benemann, 1998).
- 3 Biological water-gas shift reaction.
- 4 Photo-fermentation.
- 5 Dark fermentation: This process is able to use biomass provided by a photosynthetic solar energy conversion system to  $H_2$  production (Keasling *et al.*, 1998). Dark microbial  $H_2$  production is driven by the anaerobic metabolism of the key intermediate, pyruvate. The complete oxidation of glucose would yield a stoichiometry of 12 mol.  $H_2$  per mole of glucose, but in this case, no energy would be gained to support growth and metabolism of the producing organism (van Niel *et al.*, 2002).

In a proposed integrated system, dark fermentation and photo-fermentation are combined in order to achieve maximal conversion of the substrate to biohydrogen (deVrije and Claassen, 2002).

Starch, cellulose or hemicellulose content of wastes, carbohydrate-rich food industry effluents or waste biological sludge can be further processed to convert the carbohydrates to organic acids and then to hydrogen gas by using proper bioprocessing technologies.

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# Production of biodiesel via chemical catalytic conversion

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**Abstract:** The objective of this chapter is to provide an overview of the conversion of various lipid sources (edible and non-edible) into biodiesel using traditional and new technologies emphasizing the quality standards mainly dependent on the used feedstock and technology, processing and purification.

**Key words:** heterogeneous catalysis, homogeneous catalysis, influence of the feedstock and technology on biodiesel properties, purification of biodiesel, industrial production of biodiesel.

### 5.1 Introduction

Renewable resources and biomass are becoming major raw materials for the energy supply. Vegetable oils and animal fats are considered as sources for the green energy supply. Therefore, the demand of lipids for food (80%), feed (5%) and industrial applications (15%) such as detergents, surfactants, biolubrificants and biofuels is leading to a shortage and higher prices. During the last few years, the production of biodiesel from edible lipids has been blamed for raising the cost of food products.

Traditionally, fully refined edible oils and fats were used for biodiesel production, namely rapeseed oil in Europe, soybean oil in North and South America and palm oil in Southeast Asia. Since nearly 85% of the total production cost is originating from the feedstock cost, new starting materials, not competing with local supply, have to be explored.

The objective of this chapter is to provide an overview of the conversion of various lipid sources (edible and non-edible) into biodiesel using traditional and new technologies emphasizing the quality standards mainly dependent on the used feedstock and technology, processing and purification.

Excellent books and reviews on the production of biodiesel have been published mainly emphasizing the traditional processing (Knothe and Dunn, 2001; Verhé 2004; Knothe *et al.*, 2005; Mittelbach and Remschmidt, 2004; Mittelbach 2009; Demirbas 2009).

The use of vegetable oils, animal fats and their derivatives as a diesel fuel is nearly 100 years old. The inventor of the diesel engine, Rudolf Diesel, used peanut oil for the engine and he stated: 'vegetable oils make it certain that motor power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores solid and liquid fuels are exhausted' (Diesel, 1912). However, the use of heat in vegetable oils due to poor atomization upon injection was leading to deposits in the injection system and the cylinders, causing operational problems.

In order to reduce the viscosity, Chavanne (1937, 1943) converted a mixture of fatty acids and glycerol esters from palm oil into esters in the presence of mainly ethyl alcohol and acid catalysts. These experiments were performed in colonial Africa in order to be independent from external sources of fuels. In fact, Chavanne produced a fuel which we should call now biodiesel. In Europe, the first experiments with ethyl ester of palm oil were carried out in buses plying between Leuven and Brussels in 1938.

The word 'biodiesel' was used for the first time in 1988 (Wang) and expanded from 1991 (Bailer and De Hueber). The first plant for biodiesel was installed in 1987 in Silverberg, Austria mainly for the purpose of research at the University of Graz, by Prof. Mittelbach.

From 1990 the production of biodiesel in Europe has increased dramatically with a capacity in 2009 of nearly nine million tons per year (Fig. 5.1).

### 5.2 Biodiesel definition

Biodiesel is a mixture of fatty acid alkyl esters (FAAE) (mainly methyl esters) produced from lipids via transesterification (Fig. 5.2) of the acylglycerides or esterification (Fig. 5.3) of fatty acids.



5.1 Overview of world biodiesel production (Milke, 2009).



Theoretically 1 mol triglycerides is reacting with 3 moles alcohol producing 3 moles esters and 1 mol glycerol.

Methanol is the major alcohol used because of the lower price but other alcohols can also be used such as ethanol, isopropanol and butanol. Although the latter alcohols can give better fuel properties, they are not used on an industrial scale due to their higher price and processing problems.

Biodiesel can be produced from a variety of feedstocks including edible vegetable oils (soybean, rapeseed, palm, sunflower, palm kernel and coconut), animal fats, nonedible oils (jatropha, camelina, rice bran, pongomia, thelvetia, etc.) and side-streams from refining (soapstock, acidulated soapstock and deodorizer distillates). A future feedstock will be algae growing either in open fields or closed reactors. The yield of oil/ha is estimated to be at least ten times higher and can be produced at any place.

The cost for the production of biodiesel consists of 85% of the feedstocks. A process model to estimate biodiesel production cost has been developed. This flexible model can be modified to calculate the effects on capital and production costs of changes in feedstocks costs, changes in the type of feedstocks employed, in the value of the glycerol co-product and change in process chemistry and technology (Haas *et al.*, 2006).

According to the feedstock and technology used, a distinction is made between biodiesel from first and second generation (Table 5.1). Biodiesel of the first generation is considered as FAAE produced by the traditional alkaline catalyzed transesterification reaction from refined edible vegetable oils and animal fats. Biodiesel from the second generation is the production of fatty acid methyl esters (FAME) or other esters from resources other than edible oils and in most cases using alternative technologies. It is obvious that these resources are not in competition with food/feed production and can be considered as more sustainable and more ethical.

Biofuels from the third generation produced from lipid resources are oils and fats generating power and heat (CHP, couple heat and power) in stationary diesel engines and green diesel produced by hydrotreating of oils and fats producing linear alkanes, propane, CO, CO<sub>2</sub> and water.

	First generation	Second generation	
Final product	FAME	FAME	
Feed stock	Vegetable food oils	Vegetable oils, animal fats Used oils, high acidity oils, non-edible oils	
Technology	Alkaline transesterification	Acid esterification + transesterification (hydrocracking)	
Considerations	Food <i>vs</i> fuel conflict	Technical, non food oils	

Table 5.1 First- and second-generation biodiesel (Verhé et al., 2009)

Why are FAMEs suitable as diesel fuel? Conventional diesel fuel for transportation (DF2) is a product obtained by cracking of petroleum and consist mainly of long chain unbranched alkanes ( $C_{14}-C_{24}$ ) with a boiling range of 180–240°C, cetane number (CN) of 40–50 and heat of combustion of 45 000 kJ/kg. Biodiesel has a similar chemical structure (except for the presence of the ester function) of long chain ( $C_{12}-C_{22}$ ) with a higher boiling range (250–450°C), CN between 40 and 80 and heat of combustion of 40 000 kJ/kg. Due to the similarity in structure, CN and energy value fatty acid esters are readily replacing diesel.

Biodiesel is miscible with petrodiesel in all concentrations, namely blends B5, B20, etc. which corresponds to the percentage of biodiesel in diesel. Blend up to 20% can be used without modification of the engines. Higher blending will require modifications due to the solvent properties of the esters which are affecting the rubber tubings and fittings.

In a comparison between biodiesel and diesel the following observations can be made:

- 1. The CN for the biodiesel from soybean and rapeseed oil is slightly lower. The CN of esters correlates well with the boiling points. The CN from palm oil and animal fats are higher.
- 2. The heat of combustion is 13% lower than for DF2. However, due to the higher density there is eight per cent difference expressed in volume.
- 3. The viscosity of biodiesel is two times higher.
- 4. Biodiesel has higher cloud point (CP) and cold filter plugging point (CFPP).
- 5. Biodiesel is an oxygenated fuel which results in a cleaner burning.
- 6. Biodiesel has a higher lubricity which is advantageous in low sulfur content.
- 7. Biodiesel has a higher flash point.
- 8. Biodiesel does not contain sulfur.
- 9. Biodiesel has lower fine particulate matter, lower polyaromatic hydrocarbons and SO<sub>2</sub> emissions.
- 10. Biodiesel has higher NOx emissions.

Biodiesel can only be commercialized and sold as biodiesel on condition when it complies with biodiesel standards EN14214:2009 (EN) or ASTM D 6751 (USA). The European specifications are summarized in Table 5.2.

The most important parameters concern the ester content (minimum 96.5%) and the acid value (maximum 0.5 mg KOH/g). The ester content is influenced by the quality of the technology and processing but also by the composition of the used feedstock. The unsaponifiable fraction (sterols, tocopherols, hydrocarbons, etc.) present in the vegetable oils in a range of one to two per cent stays in the biodiesel will decrease the theoretical ester content already to 98–99%. Other important parameters are sulfur, phosphorous, alkali metals, total contamination and non-reacted acylglycerols. The CP is region dependent while there is a difference in the standard for oxidative stability between the EU and the USA (rapeseed biodiesel has a higher oxidative stability than soy biodiesel). Some of these parameters are more difficult to achieve when alternative feedstocks are used. Usage of additional pre-refining and/or post-treatment is required to guarantee the compliance with the biodiesel standards.

		EN14214	
Property	Unit	Limits (min.)	Limits (max.)
FAME content	% (m/m)	96.5	_
Density at 15°C	kg/m²	860	900
Viscosity at 40°C	mm²/s	3.50	5.00
Flash point	°C	101	-
Sulfur content	mg/kg	-	10.0
Cetane number	-	51.0	-
Sulfated ash content	% (m/m)	-	0.02
Water content	mg/kg	-	500
Total contamination	mg/kg	-	24
Oxidation stability, 110°C	hours	6.0	-
Acid value	mg KOH/g	-	0.50
lodine value	g iodine/100 g	-	120
Linolenic acid methyl esters	% (m/m)	-	12.0
Polyunsaturated (≥4 double bonds) methyl esters)	% (m/m)	-	1
Methanol content	% (m/m)	-	0.20
Monoglyceride content	% (m/m)	-	0.80
Diglyceride content	% (m/m)	-	0.20
Triglyceride content	% (m/m)	-	0.20
Free glycerol	% (m/m)	-	0.02
Total glycerol	% (m/m)	-	0.25
Group I metals (Na+K)	mg/kg	-	5.0
Group II metals (Ca+Mg)	mg/kg	-	5.0
Phosphorus content	mg/kg	-	4.0

Table 5.2 Biodiesel standard EN14214:2009 (EN)

# 5.3 Treatment of the feedstocks prior to production of the biodiesel

The majority of oils and fats after extraction (pressing, solvent extraction, combination pressing-extraction, rendering, etc.) are not suitable for the production of biodiesel, especially in large continuous plants using the traditional alkaline transesterification process. Undesirable products are non-triaclyglycerol compounds like free fatty acids (FFAs), phospholipids, oxidation products, metals, protein and carbohydrate residues, waxes, moisture and inorganic matter. Two refining routes are used (chemical and physical refining) which refer to the methodology for FFA removal.

In both refining procedures the first step is a degumming process in which the hydratable phospholipids are removed by water washing and the non-hydratable ones are discarded by treatment with citric or phosphoric acid. Enzymatic degumming becomes more attractive due to the lower losses.

In the chemical process, FFAs are removed as soaps (soapstock) by neutralization with NaOH. In the physical refining, FFAs are discarded by stripping (deodorization). Chemical refining is using a lot of water and the soapstock has to be acidified (production of acid oils) and is environmentally not recommended. In addition, there are considerable losses of lipids during the separation of the soap layer. As 85% of the production costs of biodiesel is based on the feedstock, losses should be kept to a minimum.

A bleaching step (adsorption with activated clay or silica) can be necessary for highly colored oils or high contaminated oils (removal of Ca, Fe, Cu, traces of soaps and phospholipids).

Deodorization, the last step of refining, is performed at 210–260°C, with one to two per cent steam (1 Mbar) for the removal of the FFAs and oxidation products (physical refining). In addition pigments and unwanted contaminants (PAHs are pesticide residues) are degraded. Deodorization can be omitted on condition that FFA content is very low which can be case for freshly extracted soy and rapeseed oils. A detailed overview of refining oils and fats is given by O'Brien *et al.* (2000).

A feedstock purification technology which may replace the conventional degumming process is Ambersep<sup>™</sup> B19 (amberlyst resin) developed by Daw. The product removes proteins and polysaccharides, traces of phospholipids and soaps. By doing a purification step first, the lifetime of Ambersep<sup>™</sup> B20 is extended during the esterification of FFAs in crude feedstocks.

# 5.4 Current technologies of biodiesel production

Numerous publications and patents are describing various routes for the production of biodiesel from different feedstocks. An overview is given in Mittelbach and Remschmidt (2004) and Mittelbach (2009).

Alkaline transesterification is the traditional process. Acid catalyzed transesterification is not industrially applied. However, it is seldom used in

combination with alkaline transesterification and the catalyst can be homogeneous and heterogeneous. The new developments are non-catalyzed interesterification but not industrially operational.

#### 5.4.1 Homogeneously catalyzed production of biodiesel

Today the most commercially available biodiesel production plants are using homogeneous alkaline catalyst. The reaction is a nucleophilic addition of an alkoxide anion to the carbonyl function followed by an expulsion of the glyceroxide anion (Fig. 5.4).

The catalysts used are sodium and potassium methoxides or hydroxides. The advantage of using sodium and potassium methoxides is that no water is formed



5.4 Reaction scheme for the base-catalyzed reaction.

and no saponification is occurring. The use of hydroxide involves the formation of water resulting in hydrolysis of the acylglycerides or alkyl esters with formation of soaps (Fig. 5.5).

Potassium catalysts are favorable compared to sodium catalyst due to the acceleration of the phase separation (higher density of the glycerol layer) and lower soap formation. Furthermore, salts can be used as fertilizer after neutralization with an acid. However, the price of the potassium-derivatives is higher.

In addition, due to the fact that during the reaction glycerol is separated out (glycerol has a limited solubility in lipids and biodiesel), water is also removed, shifting the equilibrium of the reaction towards alkyl ester formation. Kinetic studies of this multiple phase reaction show that the formation of the diglyceride is the slowest, whereas the next steps are much faster (Mittelbach and Trathnigg, 1990). The standard conditions for the alkaline transesterification are 6:1 molar ratio of methanol to oil, concentration of catalyst in the range of 0.5–1.5% (depending on the FFA content of the feedstocks) and temperature of 60°C.

Reaction times can be shortened using a two-step procedure or a continuous reaction with simultaneous separation of the glycerol. A typical reaction scheme involving a two-step reaction is depicted in Fig. 5.6 using potassium hydroxide as catalyst.

In the alkaline catalyzed process, it is important that the feedstock is as much as possible water-free as well as with low FFA content in order to prevent



5.5 Reaction scheme for soap formation.



*5.6* Scheme of a typical biodiesel production process according to Mittelbach and Koncar (1994) and Gutsche (1997).

hydrolysis. FFAs are not converted into esters but are transformed into soaps which cause problems in separating the glycerol layer and the water washing due to the formation of emulsions. In addition, FFAs are deactivating the catalyst with the soap formation. A feedstock with a high FFA content needs a higher concentration of catalyst. Preferably the FFA content should be less than 0.5% to ensure a complete conversion and efficient post-treatment. The glycerol layer separated from the biodiesel contains methanol, catalyst and soaps. After acidifying, the FFAs can be separated, the methanol evaporated and the sodium or potassium salts separated, purification steps which result in crude glycerol.

Biodiesel is then dried and used as such without post-treatment (if the feedstock is a refined lipid) after recovering of the excess of methanol and water washing.

Biodiesel can also be produced by transesterification of the oil *in situ*. In this procedure there is no need for the extraction of the oil from seeds. The liquid phase and solid oil containing feedstock are mixed and stirred. The disadvantage of this process is that large quantities of methanol and high concentration of catalyst are required. Furthermore, soaps are formed and additional solvent is needed to wash the seeds in order to ensure the complete separation of the oil and the transesterification reaction (Haas *et al.*, 2007; Georgogianni *et al.*, 2008; Qian *et al.*, 2008).

At 60°C, the highest yield of esters is obtained using a molar ratio 226:1:1.6 of methanol:oil:NaOH. The FFA content in the biodiesel was lower than one per cent and contains no acylglycerols. By applying a drying step of the flakes prior to the reaction, the amount of methanol and catalyst can be reduced by 50% (Haas and Scott, 2007). If the feedstock contains more than three per cent FFAs, a combination of esterification and transesterification can be used (see Section 5.4.3).

In the 'Alcohol Refining' process (Fig. 5.7) developed by Westfalia Separator (Harten, 2006), feedstocks with high FFA content can be transformed into



5.7 Alcohol refining scheme (Westfalia).

biodiesel by extraction of the FFA in the glycerol layer (still containing alkaline catalyst) separated from the alkaline transesterification step. The extracted FFAs are converted into soaps. The glycerol layer is acidified and the FFAs separated. The advantages of alcohol refining are that it provides degumming and that during the transesterification less fouling and emulsion formation is observed. The disadvantages are that the FFAs are not converted into esters (loss of yield) and that the glycerol layer (which cannot be purified economically) has to be discarded.

The addition of solvents such as tetrahydrofuran and methyl *t*-butyl ether can accelerate the transesterification due to an increased solubility of methanol in the oil (Boocock *et al.*,1998). Another alternative to prepare biodiesel involves the application of microwave irradiation (Breccia *et al.*, 1999) and ultrasonic irradiation (Stavarache *et al.*, 2003).

Microwave heating looks very promising for a continuous flow preparation using a commercially available scientific microwave apparatus. The methodology allows for the reaction to be run under atmospheric conditions with flow rates up to 7.2 L/min, using a 4 L vessel. It can be utilized with methanol 1:6 molar ratio of oil:alcohol (Barnard *et al.*, 2007).

The apparatus can be also used with butanol and sulphuric acid or potasium hydroxide as catalyst (Leadbeater *et al.*, 2008).

A novel laminar flow biodiesel reactor/separator has been developed achieving high conversion rate while simultaneously allowing glycerol to separate and to settle from the reaction flow. At 40–50°C, a feed of 1.2 L/min (1:6 oil:methanol molar ratio) and 1.3% potassium hydride, a 99% conversion of waste canola oil was achieved with the removal of 70–99% of produced glycerol (Boucher *et al.*, 2009).

#### Acid transesterification and esterification

Transesterification can also be performed in the presence of strong acid catalysts such as sulfuric acid and p-toluene sulfonic acid, normally for feedstocks with high FFA (>0.5%) (Fig. 5.8).

Methanesulfonic acid has been introduced by BASF (Lutropur®) as an efficient catalyst for esterification of low quality oils. This acid is less corrosive, non-oxidizing and more environmentally friendly than sulfuric or phosphoric acid. It is also used as a neutralizing agent in this base-catalyzed transesterification.

The advantage of this process is that FFAs are simultaneously converted into esters. Therefore, acid-catalyzed transesterification can be used for feedstocks which are containing high amounts of FFAs such as crude palm oil (up to 8%), used frying oils (3–7%), animal fats (up to 30%), grease and side-streams from oil refining (10–90%).

The mechanism involves protonation of the carbonyl function giving rise to a carbonium ion which is attached by the nucheophilic alcohol followed by splitting of the diglyceride and the aliphatic ester. The reaction is repeated with the diglyceride and monoglyceride. Acid transesterification has a number of disadvantages:

- Acid catalyzed transesterification is much slower than alkali catalysis (Canacki 1999).
- Due to the slow reaction rate higher temperatures and pressure have to be applied (100°C/5 bar) which can also result in formation of by-products (formaldehydes and glycerol ethers).
- Feedstocks containing 0.5% water give rise to a yield decrease of one to five per cent (Canacki 1999).
- During the esterification water is formed which causes hydrolysis of the triglycerides resulting in lower yields.



5.8 Acid-catalyzed transesterification and esterification reactions.

• The most employed acid catalyst (sulfuric acid) is very corrosive and causes dark colouring of the produced biodiesel.

The most economical conditions involve the use of molar ratio of 20:1 of methanol:oil, three per cent of sulfuric acid at 65°C for 48 hours. A comparison of base and acid catalyzed transesterification with methanol (with KOH and  $H_2SO_4$  as catalysts) has also been reported (Nye *et al.*, 1983).

The reaction kinetics of acid catalyzed transesterification of used frying and cooking oils has been studied by Zheng *et al.*, (2006). The oil:methanol molar ratio and the temperature were the most significant factors influencing the conversion. Using a large excess of methanol and oil:methanol:acid ratio of 1:245:38 at 70°C and respectively a ratio of 1:75:1.9 at 80°C, gave a conversion of 99% in ca. 4 hours (pseudo-first-order kinetics). However, large scale production may not be economically feasible due to the large excess of methanol employed. It was reported that waste palm oil has also been transesterified in acid conditions (Al-Widyan and Al-Shyoukh, 2002).

Other homogeneous catalysts which can be used are phosphoric acid, hydrogen chloride, sulfonic acids and Lewis acids  $(BF_3, SnCl_2, AlCl_3, FeCl_3, CaCl_2)$  (Mittelbach and Trathnigg, 2004).

Other promising catalysts are acetates and stearates of calcium, barium, magnesium, mangane, cadmium, bad, zinc, cobalt and nickel. A ratio of oil:alcohol of 1:12 at 200°C for 200 minutes is used. Stearates gave better yields due to higher solubility in the lipophilic phase. The advantages of these catalyst in comparison with Brønsted acids are the lower alcohol used and a less sensitivity towards the content of water in the feedstock (Di Serio *et al.*, 2005).

In addition *in situ* acid catalyzed transesterification were successfully performed. Using sulfuric acid *in situ* transesterification of homogenized sunflower seeds, an esters yield up to 20%, greater than with extracted oil, was reported due to the transesterification of the seed with lipids (Harrington and D'Arcy-Evans, 1985; Siler-Marinkovic and Tomasevic, 1998).

Similar processes have been used for rice bran oil (Özgül-Yücel and Türkay, 2002). Recently, an acid catalyzed *in situ* transesterification of soybean oil in carbon dioxide expanded methanol was published (Wyatt and Haas, 2009). A 1.2 N sulfuric acid solution in methanol containing 50% mol fraction  $CO_2$  resulted in a 90% conversion of the triacylglycerol within 10 hours. Introduction of  $CO_2$  into the system increases the rate of reaction 2.5-fold. Alkaline transesterification in gas expanded methanol was unsuccessful.

Tin(Sn<sup>2+</sup>) complexes using the liganol 3-hydroxy-2-methyl-4-pyronate (maltolate) have been used to convert various vegetable oils into FAME at 80°C using a molar ratio of 400:100:1 of methanol:oil:catalyst. Yields up to 90% can be obtained but the methanolysis is dependent on the nature of acid chain favoring the presence of unsaturation and chain length. Technological potential is rather low as the complexes remain dissolved in the reaction medium. Attempts have been made to immobilize the complexes (Suarez *et al.*, 2008).

#### Combined esterification-transesterification

A single acid or alkaline catalysis is not efficient to produce alkyl esters meeting the EU and US biodiesel standards if crude oils, fats and waste oils are being used. Therefore, a combined process with both acidic and alkaline catalyst in a two step reaction is required in which the acid treatment convert soaps and FFA into esters while the alkaline catalyst converts the acylglycerides into esters.

A dual process (Fig. 5.9) has been developed by Canacki and Van Gerpen (2003). A batch reactor was used to produce biodiesel from crude soybean oil, yellow grease (9% FFA) and brown grease (40% FFA). The high FFA feedstocks are firstly esterified with  $H_2SO_4$  to reduce the FFA content to 1%, followed by transesterification with methanol and KOH.

The reaction rate is dependent upon the concentration of methanol and is increased if higher concentrations of  $H_2SO_4$  are used. A ratio of methanol:oil (40:1) is used for feedstocks with high FFA content in comparison with the 6:1 ratio in alkaline catalysis. Replacing methanol by ethanol shows faster acidic esterification. Similar processes have been developed by Issariyakul *et al.* (2007) using a mixture of methanol/ethanol.

A more efficient procedure to convert high acidic feedstocks using short chain alcohols and a combination of acidic esterification and an alkaline process in the presence of ethylene glycerol and glycerol (temperature lower than 120°C and pressure lower than 5 bar) was described by Lepper and Friesenhagen (1986). Due to the immiscibility with the lipophilic layer, the water formed is entrained.



*5.9* Production of biofuels from recovered oil and from frying oils (Canacki and Van Gerpen, 2003).

The acid treated oil containing fatty acid esters and mono- and diesters of ethylene glycol and glycerol is treated with alkaline catalyst for the transesterification. The advantage of the process is a short reaction time due to the continuous removal of the water and no soap formation is taking place. The disadvantage is the removal of the catalyst which requires two separations if the acidic catalyst has not been neutralized by an additional amount of alkaline catalyst. Canacki and Van Gerpen (1999) stated that using in feedstocks like crude and waste oil can result in a 25% reduction in cost relative to fully refined edible oils. However, Zhang *et al.* (2003) explained that it seems not to be clear. The traditional alkaline process requires the lowest fixed capital cost, but a much higher feedstock cost. The acid–alkaline process has a lower manufacturing cost, an attractive tax return (green certificates) and a lower biodiesel breakeven price. On the contrary, the corrosive nature of the acid catalysts should be included in the economic evaluation.

Biodiesel from low grade animal fat mixed with soybean oil has been synthesized in a combined esterification and transesterification process. A mixture of 50% of both raw materials has been selected and a computer simulation of the production process using Aspen Plus software has been carried out to evaluate the industrial feasibility. The acid esterification was performed with p-toluene sulfonic acid instead of sulfuric acid. The use of the latter one can cause a high concentration of sulfur in the biodiesel. However, the reaction rate is much faster than the reaction rate with p-toluene sulfonic acid (Canoira *et al.*, 2008).

A variant of the acidic alkaline process is an alkaline transesterification followed by an acidic esterification on condition that the feedstock is containing maximum ten per cent FFAs (Verhé *et al.*, 2009). Higher acid concentrations deactivate the alkaline catalyst in a too large extent. Both reactions are carried out in one reactor without intermediate separation of the layers (Fig. 5.10).



5.10 Schematic representation of the process for the conversion of crude palm oil (CPO) to biodiesel (Verhé *et al.*, 2009).

Reaction steps:

- 1. Neutralization of FFA and alkaline transesterification
- 2. Acidic esterification
- 3. Evaporation of methanol
- 4. Separation of glycerol layer
- 5. Washing of biodiesel with water.

Reaction conditions:

- Alkaline transesterification:
  - catalyst 0.6% KOCH<sub>3</sub> (33% in CH<sub>3</sub>OH) + calculated amount of KOCH<sub>3</sub> in order to neutralize the FFA
  - methanol: 20%
  - temperature: 65°C
  - reaction time: 90 minutes
- Acidic esterification:
  - catalyst: 2% H<sub>2</sub>SO<sub>4</sub> + calculated amount to neutralize the excess of KOCH<sub>3</sub> and split the soaps
  - temperature: 65°C
  - reaction time: 180 minutes

The oil is heated at 65°C and mixed with the alkaline catalyst and methanol. Without separation of the glycerol that calculated amount of  $H_2SO_4$  is added. After 3 hours, the methanol is stripped off and the crude biodiesel is transferred to a separator for glycerol removal. Water is added and the glycerol/water layer is separated. The biodiesel is washed with water until neutral and dried at 65°C under vacuum.

The main advantage of this process is that the feedstock does not require a prerefining for the removal of the phospholipids, gums, traces of proteins and carbohydrates. During the esterification and work-up in acidic conditions at 65°C, a degumming is occurring, pigments are decomposed and are discarded with the aqueous layers. Separation of the glycerol and aqueous layers is much easier in acidic medium as no emulsions are formed. During the acidic esterification the residual acylglycerols are also transesterified into FAMEs resulting in higher conversion rates.

# 5.4.2 Heterogeneously catalyzed production of biodiesel

Although homogeneous catalysis is the traditional and very efficient process to convert lipids into alkyl esters, it has a number of disadvantages. The catalyst cannot be reused and has to be discarded after the reaction. In addition, catalyst residues have to be removed from crude biodiesel using several water washing steps that increases the production cost and complicates the purification of the glycerol. Recently an excellent review was published dealing with heterogeneous catalyst for biodiesel production (Di Serio *et al.*, 2008). Various processes are available using heterogeneous catalysts which are simplifying the purification costs of the biodiesel and the glycerol. The advantage of heterogeneous catalysis is that the catalyst can be either recovered by filtration and/or decantation or applied in a fixed bed reactor and the post-treatment of the biodiesel and glycerol is easier.

#### Heterogeneous alkaline catalysis

Many heterogeneous alkaline catalysts are available but the most frequently used are alkali metal, alkaline earth and metal salts. An overview is given in Table 5.3 (Bacovsky *et al.*, 2007).

Heterogeneous basic catalysts can be classified as Brønsted or Lewis catalyst. As in the case of homogeneous Brønsted basic catalyst such as basic zeolites, the formed catalytically active compound is a homogeneous alkoxide (Fig. 5.11) (Lotero *et al.*, 2006).

In the case of heterogeneous Brønsted basic catalysts (e.g. resins with quaternary ammonium functions,  $QN^+OH^-$ ), the positive organic ammonium groups being bonded to the support surface electronically retain the catalytic anion on the solid surface.

Catalyst type examples				
Alkali metal carbonates and hydrogen carbonates	Na <sub>2</sub> CO <sub>3</sub> , NaHCO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub> , KHCO <sub>3</sub>			
Alkali metal oxides	K <sub>2</sub> O (produced by burning oil crop waste)			
Alkali metal salts of carboxylic acids	Ca-laurate			
Alkaline earth metal alcoholates	Mixtures of alkali/alkaline earth metal oxides and alcoholates			
Alkaline earth metal carbonates	CaCO <sub>3</sub>			
Alkaline earth metal oxides	CaO, ŠrO, BaO			
Alkaline earth metal hydroxides	Ba(OH) <sub>2</sub>			
Alkaline earth metal salts of carboxylic acids	Ca- and Ba- acetate			
Strong anion exchange resins	Amberlyst A 26, A 27			
Zinc oxides/ aluminates				
Metal phosphates	Ortho-phosphates of aluminum, gallium or iron (III)			
Transition metal oxides, hydroxides and carbonates	Fe <sub>2</sub> O <sub>3</sub> (+ Al <sub>2</sub> O <sub>3</sub> ), Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub> , FeOOH, N <sub>1</sub> O, Ni <sub>2</sub> O <sub>3</sub> , NiCO <sub>3</sub> , Ni(OH) <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>			
Transition metal salts of amino acids	Zn- and Cd-arginate			
Transition metal salts of fatty acids	Zn- and Mn-palmitates and stearates			
Silicates and layered clay minerals	Na-/K-silicate			
	Zn-, Ti- or Sn- silicates and aluminates			
Zeolite catalysts	Titanium-based zeolites, faujasites			

#### Table 5.3 Overview on heterogeneous catalysts (Bacovsky et al., 2007)

5.11 Reaction mechanism for heterogeneous catalysis (I).

The reaction occurs between the methanol adsorbed on the cation and the ester from the liquid (Fig. 5.12).

$$|$$
  $O^-N^+OH^-$  +  $CH_3OH$   $\longrightarrow$   $O^-N^+OCH_3^-$  +  $H_2O$ 

5.12 Reaction mechanism for heterogeneous catalysis (II).

The formation of alkoxide functions is the fundamental step for heterogeneous Lewis basic catalyzed reactions. In the case of MgO, the reaction occurs between the methanol molecules adsorbed on magnesium oxide free basic sites and the esters functions in the triglycerides in the liquid phase (Fig. 5.13).

In the review by Di Serio *et al.* (2008) many applications of heterogeneous alkaline catalyst have been described.



5.13 Reaction mechanism for heterogeneous catalysis (III).

In comparison with homogeneous catalysts, in order to obtain similar conversion rates, more severe reaction conditions have to be used:

- Temperatures up to 300°C under supercritical conditions are a pre-requisite to achieve conversions higher than 90%.
- High molar rates methanol:oil have to be utilized: 15–40:1.
- Longer reaction times (except in methanol supercritical conditions or microwave irradiation).
- Higher amounts of catalyst.
- Leaching of the catalyst into the biodiesel.

Good results using alkaline-earth metal hydrides, oxides and alkoxides have been reported by Gryglewicz (1999) and Demirbas (2007). The order of reactivity  $Ca(OH)_2 < CaO < Ca(OCH_3)_2$  is in agreement with the Lewis theory stating that methoxides of alkaline-earth metals are stronger bases than the corresponding oxides and hydroxides. Good biodiesel yields were also obtained in the transesterification of soybean oil using ZnO, loaded  $Sr(NO_3)_2$  followed by calcination. The active catalyst is SrO. When the reaction is carried out at reflux, five per cent catalyst and 12:1 mol ratio of methanol:oil, a conversion of 95% can be reached (Lopez Granados *et al.*, 2007).

The preparation of new materials obtained from the co-precipitation of aluminum, tin and zinc oxides and their use as catalytic systems for the alcoholysis of vegetable oils have been reported by Macedo *et al.*, 2006. These  $(Al_2O_3)_X$  (SnO)<sub>Y</sub>(ZnO)<sub>Z</sub> type of metal-oxides were found to be active for the alcoholysis of soybean oil, using several alcohols, including branched ones. Best results were achieved using methanol, with conversion yields up to 80% in 4 hours. It was also possible to recycle the catalysts without apparent loss of activity.

Sodium silicates can be used at  $60-120^{\circ}$ C but the use of microwave energy greatly increases the conversion (Portnoff *et al.*, 2006).

Good results have also been obtained by  $MgO/Al_2O_3$  hydrotalcites and industrial applications could be possible if the reaction was carried out at 180°C and 12:1 methanol:oil molar ratio (92% yield) (Leclercq *et al.*, 2001; Di Serio *et al.*, 2006).

Waste oil was converted in good yields using Mg-Al layered double hydroxide catalysts in 80–160°C temperature range with up to 48:1 molar methanol:oil ratio and high amounts of catalyst (up to 12%) (Brito *et al.*, 2009).

In addition calcined Li-Al layered double hydroxides (Shumaker 2007), sodium zeolites, titanium containing zeolites (Xie *et al.*, 2007), anion resins (Shibasaki-Kitakawa *et al.*, 2006) and polystyrene supported guanidine and biguanidines (Gelbard and Vielfaure-Joly, 2001) have shown promising results.

The use of strong alkaline ion exchange resins is limited due to the loss of stability at temperatures higher than 40°C and the neutralization of the catalyst by the FFA present in the feedstock.

In addition, the glycerol formed is absorbed in the polymeric matrix causing deactivation of the active sites.

Very recently, an efficient laboratory procedure has been developed using CaO after appropriate treatment which allows reaching high conversions of triacylglyceride (TAG) into FAME in a one-stage operation, meeting the requirements of the EN 14214 (Kouzu *et al.*, 2008; Lengyel *et al.*, 2009). The catalyst was activated by drying for 24 hours at 105°C. Using 6:1–12:1 molar ratio of methanol:oil, reflux temperature and eight per cent catalyst, conversion rates of 99% were obtained. However, organosols are formed due to the presence of calcium soaps, leading to a yield of 70%.

An industrial applied heterogeneous catalysis process (Fig. 5.14) has been selected by Diester Industrie using Axens biodiesel technology, Esterfip- $H^{TM}$  for a new plant in Sète (France) with a capacity of 160 000 tonnes per year, followed by a plant in Sweden in 2007. The catalyst consists of a mixed oxide of Zn and Al coated on  $\gamma$ -alumina, which promotes the transesterification without catalyst loss. The reaction is performed at higher temperatures and pressures compared to those of homogeneously catalyzed processes, also using an excess of methanol. This



5.14 Esterfip-H simplified process flow diagram (www.axens.net).

methanol excess is removed by vaporization and reused in the reaction together with the fresh methanol. The conversion is reached in two successive stages and separation of the glycerol in order to shift the equilibrium to methanolysis.

The catalyst section includes two fixed bed reactors. Excess of methanol is removed after each reactor by partial evaporation and the esters and glycerol are separated in as settler. The residual methanol in the glycerol is evaporated. Biodiesel purification consists of methanol vaporization under vacuum and adsorption of the soluble glycerol (Bournay 2005).

The advantage of the process is a very high biodiesel quality, salt-free glycerol, no soaps formation and no handling of hazardous chemicals. This process can be considered as green technology.

On a semi-industrial scale a new type of heterogeneous catalyst has been introduced by Catalin using nanoparticles. The catalyst preparation involves the utilization of organotrialkoxysilanes with various anionic, hydrophobic or hydrophilic functional groups that could provide different noncovalent interactions, for example electrostatic attractions, hydrophobic interactions etc., with cationic cetyltrimethylammonium bromide (CTAB) surfactant micelles in a base catalyzed condensation reaction of tetraethoxysilane.

Catalin T300 catalyst differs from the most solid catalyst that requires a fixed bed and high temperature and pressure to operate. The T300 catalyst can be used in existing plants with minimal modification as it reacts at common operational temperatures and pressure. The reactor consists of a reactive vessel within a plate with a mesh. The catalyst is stocked on top of the mesh and the oil flows through. The T300 catalyst is a 'drop-in catalyst' that can be used as a direct replacement for the commonly used sodium methoxide. Therefore there is no need for a fixed bed and the catalyst in the form of a granular powder can be directly mixed with oil.

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5.15 Catalin process flow diagram (Catalin, 2009).

A filter system is used to keep the catalyst in the reactor and there is no need for water washing. The Catalin process flow diagram is depicted in Fig. 5.15.

#### Heterogeneous acid catalysis

Acid catalysis is simultaneously performing esterification of FFAs and TAGs. In this way, it is more economical to use low-quality feedstocks and lower processing costs.

The reaction mechanism using solid Brønsted acids catalyzed esterifications is similar to that of the homogeneously catalyzed process. The reaction involves a nucleophilic attack of the adsorbed carboxylic acid with the free alcohol in the rate-determining step. The formation of a more elecrophilic intermediate is also occurring with solid Lewis acids. The rate-determining step is dependent on acid strength. If the strength of the acid sites is too high, the desorption of the ester is decreased. This mechanism is valid for both homogeneous and heterogeneous catalyst (Bonelli *et al.*, 2007).

Many studies for the heterogeneous acid esterification have been carried out, mainly using acid resins (Lotero *et al.*, 2006).

Lopez (2006) has tested the activity of various acid catalysts in the transesterification of triacetin at 60°C. The flowing order of activity was observed:  $H_2SO_4 > Amberlyst-15$  (polystryrenesulphonic acid resin) > sulfated zirconia > Nafion NR-50 (perfluorinated alkanes resin sulfonic acid) > tungstated zirconia B > supported phosphoric acid > zeolite B.

The remarkable low activity is due to diffusion limitations in the zeolite pores of the bulky TAGs. At low temperatures the transesterification activity is slow and in order to obtain high reaction rates the temperature has to be increased above 170°C. However, many sulphonic acid catalysts are unstable at these high temperatures and therefore lower temperatures have to be used (120°C). Esterification is an equilibrium reaction and a nearly complete ester formation can only be reached after stripping off the water and adding additional methanol (Pasias *et al.*, 2006).

An industrial process for the conversion of FFAs into FAMEs using heterogeneous catalyst (e.g. acid Amberlyst<sup>TM</sup> BD20), called FACT (Fatty Acid Conversion Technology) has been described by Soragna (2008).

The process involves a continuous, counter-current, multiple-step esterification using a solid catalyst in fix bed reactors at 90°C and 3.5 bar with intermediate methanol recovery. Production of biodiesel is performed by direct conversion as 'stand-alone process' where the quality of the FAMEs are increased by distillation or by an 'integrated process' where the ester content is increased by transesterification of the residual acylglycerols. A schematic representation of these two processes has been discussed later in this book (Chapter 22). High acidity feedstocks such as animal fats, used cooking oils, fatty acid distillates and high acidity vegetable oils can be used.

Esterification of FFAs in waste cooking oils was studied by Özbay *et al.* (2008). The highest FFA conversion (46%) was obtained over a strong acidic macroreticular ion-exchange resin A-15 at 60°C with two per cent catalyst. Conversion of FFAs increased with increasing temperature and catalyst amount.

A comparative study of different heterogeneous catalyst (Dowex Monosphere 550A and zeolites NaY, VOx over USY) and different alcohols with oleic acids show FFA conversion of 51%. Enzymatic esterification is looking more promising (Marchetti and Errazu, 2008).

Superiority of physical properties of resins may be a dominant factor for high activity. Other acid catalyst A-16, A-35 and Dower HCR-W2 are less active.

Similar results have been obtained by Marchetti *et al.* (2007), showing that reuse of the catalyst results in low conversion rates. A general overview of the production from acidulated soapstock (acid oil) has been described by Luxem and Mirous (2008) emphasizing various processes using homogeneous and heterogeneous catalyst, mainly converting FFAs to FAME (87–92%) with 20% catalyst, a ratio of methanol to FFA of 3.8:1 and 3.5 hours.

Tin  $(Sn^{2+})$  complexes using the ligand 3-hydroxy-2-methyl-4-pyronate (maltolate) have been used to convert various vegetable oils into FAME at 80°C using a molar ratio 400:100:1 of methanol:oil:catalyst.

Yields up to 90% can be obtained but methanolysis is dependent on the nature of acid chain favoring the presence of unsaturation and chain length. Technological potential is rather low as the complexes remain dissolved in the reaction medium. Attempts have been made to immobilize the complex (Suarez *et al.*, 2008).

A combined acid esterification and alkaline transesterification using a base and acid functionalized mesoporous silica nanoparticles has been proposed by Huang *et al.* (2008). These nanoparticles contain base (primary amines) and sulfonic acids inside the porous channels and are employed for one-pot reaction cascades.

# 5.4.3 Non-catalytic production of biodiesel

A non-catalytic process for the production of biodiesel has a number of advantages over the conventional alkaline-catalyzed alcoholysis. In conventional processes FFAs and water have to be removed as they are decreasing the catalyst activity. In addition the post-treatment is more easy and economic and is leading to a glycerol stream of high purity. Supercritical methanol has been used for the direct transesterification. The first experiments were performed by Saka and Kusdiana (2001), followed by Demirbas (2002, 2003) and Madras *et al.* (2004). In a typical experiment, the reaction takes place at 350–400°C at a pressure of 45–60 MPa for a reaction time of 7–15 minutes giving a yield of 98% FAME.

The higher conversion rate in comparison with the catalytic process is the formation of single methanol/oil mixture in critical state due to the lower dielectric constant of methanol in supercritical state instead of the normal two-phase state.

Another advantage is that also the FFAs are converted into methyl esters and the water content is not affecting the conversion (Demirbas, 2008). The rate of ester formation is much higher for TAGs. In this way, supercritical methanol is very suitable for the transformation of waste oils and crude oils with high FFA content.

Parameters affecting ester formation are reaction temperature (the conversion is higher at 350°C than at 400°C), pressure, molar rate, water and FFA content. The molar ratio of alcohol:oil is normally in the range 20–40:1.

The non-catalytic supercritical methanol transesterification is performed in a stainless steel cylindrical reactor (autoclave). The autoclave is charged with vegetable oil and methanol. After each run, the gas is vented and the reaction mixture is poured into a vessel.

Non-catalyzed production of biodiesel using supercritical alcohols has been developed.

A two-stage continuous biodiesel process with supercritical water and methanol has been reported. A mixture of the oil and methanol are introduced in a reactor at 1 atm and 25°C. In the first reactor, the TAGs are hydrolyzed into FFAs at 10 MPa and 170°C and the acids are rapidly converted into FAMEs under supercritical conditions. The methanol is distilled off, and by reducing the pressure the glycerol can be separated after which the oil is transferred to a final supercritical reactor (Minami and Saka, 2006).

Catalytic supercritical methanol transesterification can be carried out in the presence of one to five per cent NaOH, CaO or MgO at 247°C. The yield of conversion is extremely fast: 60–90% in the first minutes. However, the oil must contain less than 1% FFA.

A technology using superheated methanol vapour has also been reported. This vapour is blown into oil to generate FAMEs together with the excess of methanol vapour, followed by condensation. The reaction is performed under atmospheric pressure which is reducing the cost. The optimum reaction temperature balance has been made by Ishikawa *et al.* (2005) and shows lower production costs than the conventional alkaline process (Fig. 5.16).

transesterification/cracking Simultaneous reaction under supercritical conditions denoted as STING (Iijima et al., 2007) has also been developed. In this process, transesterification and cracking proceed simultaneously and TAG, DAG, MAG and FAME, which consists of medium chain fatty acid, higher/ lower alcohols and other hydrocarbons, are formed without the formation of by-products (e.g. glycerol) improving in this way the yield of the process. A mixture of oils or fats (70%) and methanol (30%) were reacted at 460°C, 20 MPa for 5 minutes. The resulting product has a lower viscosity and lower pour point compared to FAME formed by a conventional alkaline catalyzed process, mainly because part of the long chain fatty acids ( $C_{14}$  to  $C_{22}$ ) are decomposed into the short or middle chain fatty acids (mainly  $C_6$  to  $C_{10}$ ) by treating with supercritical methanol. These components form one phase and are used as a diesel fuel replacement.

A disadvantage of supercritical production of biodiesel from oils with a high concentration of polyunsaturated fatty acids is the occurrence of thermal degradation reactions (Imakara *et al.*, 2008).

At 350°C/43 MPa, unsaturated FAMEs are partly decomposed reducing the yield and cis-trans isomerisation reactions take place. Only 20% of methyl



*5.16* Flow chart of energy and materials of large scale non-catalytic reactor, based on the supercritical methanol vapor bubble method (lshikawa *et al.*, 2005).

linoleate was recovered after 20 minutes and an average number of 2.7 *trans*-type bonds were formed. However, the transformation does not affect the cold flow properties of the final biodiesel obtained. Oxidation reaction with formation of hydroperoxides results in a lower density and combustion heat (Demirbas, 2007).  $N_2$  addition has been shown to contribute to an improvement in the oxidative stability and reduction of the total glycerol content at the transesterification equilibrium (Imakara *et al.*, 2009).

Another phenomenon observed is the transformation of glycerol into smaller molecules and water in supercritical biodiesel production at 280°C and molar ratio of methanol:oil is 15:20. This water reacts with the triglycerides to form FFAs which are transformed into FAMEs by simple esterification (Aimaretti *et al.*, 2009).

Another non-catalytic process is the BIOX co-solvent process (www.bioxcorp. com). BIOX is a combination of esterification of the FFAs (first reaction) and transesterification of the glycerides (second reaction) through the addition of a co-solvent (tetrahydrofuran) in a two-step, single-phase process at atmospheric pressure and ambient temperatures, within 10 minutes. It is a very fast reaction using feedstocks such as used cooking oils and animal fats (Van Gerpen *et al.*, 2004).

# 5.5 Purification of biodiesel

FAMEs production that meet specifications and standards can be easily obtained using refined vegetable oils or animal fats and the appropriate processing conditions. However, when alternative feedstocks are utilized including cooking oils or non-refined oils/fats, a post-treatment is required in order to reach standard properties.

Three different post-treatments are most generally employed in this regard: distillation, adsorption and filtration. The most effective is biodiesel distillation in order to remove non-volatile contaminants such as steryl glucosides, phospholipids, soaps, dimeric and polymeric materials and inorganic salts. However, the distillation has to be performed at ca. 200°C at 1 Mbar which is not an energy-friendly operation. The refining of biodiesel via vacuum distillation is illustrated by using used cooking oils (Ensungur, 2008; Zyaykina *et al.*, 2009). In the refining step, a number of polar dimeric, polymeric and oxidation compounds have been formed together with the FFAs, di- and monoglycerides and *trans* fatty acids, while dimeric and polymeric FAMEs are generated during transesterification. Accordingly, the biodiesel obtained in this process will have a high viscosity and a very low oxidative stability. Used cooking oil containing 24% polar compounds was transesterified producing a biodiesel with a viscosity of 6.4 mm<sup>2</sup>/s. After distillation, the viscosity was reduced to 3.7 mm<sup>2</sup>/s. However, the oxidative stability was further reduced from 3.3 hours (before distillation) to 1.5 hours (after distillation).

Distillation is lowering the viscosity below the maximum limit but at the same time the oxidative stability is decreased as the natural anti-oxidants (tocopherols)

are not distilled and remain in the distillation residue. Addition of synthetic antioxidants is necessary to reach to oxidative stability of 6 hours.

Distillation has however a favorable influence on the cold filtration properties of biodiesel (cold soak filter test and filter plugging point) due to removal of mono-, diglycerides and steryl glucosides during distillation.

In future, due to the expected high stringent standards, distillation is looking the most favorable process to produce biodiesel in compliance with all the standards and quality demands. Adsorption by magnesium silicate was also reported as an efficient procedure in order to upgrade the biodiesel quality (Bertram *et al.*, 2009).

Table 5.4 shows the results of dry washing with 1% Magnesol®R60, at 70°C for 20 minutes, followed by filtration.

The most important result is that the heated biodiesel contained lower soap content and had higher oxidative stability. Similar results have been obtained for rapeseed oil and yellow grease feedstock. Biodiesel can also be purified by cellulose derivatives produced by Rettenmaier. Filtracel®EFC plus are silica gel encapsulated fibers combining the excellent filterability of cellulose filter aids with the excellent adsorption properties of silica gel in just one product.

It works as filter aid and adsorbent to remove soaps, trace metals, phospholipids and other polar oil contaminants, being more efficient than bleaching earth. Some Filtracel grades have been additionally activated by citric acid which chelates non-hydratable soaps, phospholipids and metals by converting them into a hydratable form for adsorption. These cellulose derivatives are acting as desiccant and also remove hazy cloudiness. Biodiesel is chilled to crystallize free sterol glucosides, which are removed by filtration.

Parameter	Unwashed, untreated FAME	1% Magnesol®R60 treated FAME	Washed and dried FAME
Acid number, mg KOH/g	0.32	0.27	0.31
Oxidative stability at 110°C, h	0.5	3.7	0.2
Viscosity at 40°C, mm²/sec	4.1	4.1	4.2
Metals Na, mg/kg	3	<1	5
Metals Ca + Mg, mg/kg	0	0	0
Carbon residue, %	<0.01	<0.01	0.05
Total glycerine, %	0.21	0.19	0.20
Free glycerin, %	0.03	<0.01	<0.01
Methanol content, %	0.11	0.01	<0.001
Soap, mg/kg	651	4	13
Phosphorus content, mg/kg	<1	<1	<1

Table 5.4 Results for soybean oil biodiesel

# 5.6 Industrial production of biodiesel

Biodiesel can be produced on industrial scale using a batch or continuous process. The most suitable oils are produced from soybean (USA, Latin America), rapeseed (EU) and palm (Southeast Asia) oils. Refined vegetable oils are the best resource due to the high conversion of triglycerides into esters in a short time of reaction. Nearly only methanol is used to the lowest price and the easiest production process is employed. The most commonly used catalysts are NaOH, KOH, NaOCH<sub>3</sub> with a loading in the range between 0.3% and 1%. The operating temperature is  $60-70^{\circ}$ C and molar ratio of CH<sub>3</sub>OH:oil is 6:1. In a batch process, the oil is charged in the reactor followed by the catalyst and methanol addition. After stirring, the reaction mixture is settled, centrifuged or pumped to another vessel in order to separate the glycerol layer from the biodiesel. The methanol is recovered from the ester layer and glycerol by flash evaporation.

The ester is neutralized by diluted acid, washed with water and dried under vacuum. The glycerol is neutralized, the FFAs separated and eventually refined for further use. In many cases the batch process is carried out in a two-step reactor.

An example of this is the Lurgi technology, in which most of the glycerin is separated at the first reactor supplied with esterification column for the separation of the excess of methanol and glycerin. Biodiesel produced after the second reactor is treated in a wash column to remove the glycerin and methanol.

Biodiesel production can also be carried out in a continuous process using tubular system as in the Desmet Ballestra biodiesel technology. This technology is characterized by its integrated feedstock pre-treatment and transesterification. Crude oils and fats are first pretreated to meet certain preset quality standards and are then processed in the standard transesterification process. This approach allows the processing of a whole range of feedstocks, including traditional biodiesel feedstocks (rapeseed, soybean, palm oil and sunflower) but also alternative and/or lower quality feedstocks (animal fat, used cooking oil, jatropha oil, etc.). A typical Desmet Ballestra biodiesel plant configuration (including pre-treatment section) is outlined in Fig. 5.17.

The Desmet Ballestra biodiesel process technology uses three reactors in series which operate under mild conditions (temperature of  $55^{\circ}$ C and atmospheric pressure) (Fig. 5.18). Pre-treated feedstock is continuously fed to the first loop reactor 1 together with methanol and catalyst (NaOCH<sub>3</sub>). Methanol is added in a proper excess compared to the required stoichiometric amount in order to maximize the degree of transesterification and to minimize soap formation. Loop reactor 1 has a settling zone in the bottom part from which spent glycerin is continuously discharged. The reacted light phase overflows to the second loop reactor 2 where fresh methanol and catalyst are added. Loop reactor 1 and 2 are identical and operate under the same conditions. The light phase leaving the



5.17 Desmet Ballestra biodiesel process.

second loop reactor consists of almost fully converted biodiesel. It is transferred to a third stirred-tank (safety) reactor in which the final conversion takes place.

# 5.7 Influence of the feedstock and technology on biodiesel properties

The quality standards, fuel properties and performance of biodiesel are determined by the nature and quality of the feedstock, the pre-treatment and yield and the efficiency of transesterification reaction, the technology used and eventually the



5.18 Transesterification unit (Desmet Ballestra).

post-treatment. Extended reviews on the fuel properties have been recently reported (Knothe 2005; Erhan 2008).

# 5.7.1 Influence of the nature of the feedstock

The nature of the feedstock is influencing a number of parameters such as the ester content, CN, CP/CFPP, viscosity and the oxidative stability. However, there is little influence on the heat of combustion, flash point, lubricity and emission. The ester content of the biodiesel is dependent on the feedstock due to the presence of FFAs which are not converted into esters, the amount of unsaponifiable fraction (1-2%) which is not removed during reaction and impurities such as dimers and polymers of TAG which are transformed into dimeric and polymeric alkyl esters.

The physical properties of biodiesel are mainly influenced by the fatty acid composition of the feedstock (see Chapter 4 for more details).

The melting point (MP) of FAME is mainly dependent upon the fatty acid alkyl chain:

- The longer the alkyl chain length the higher MP
- Presence of unsaturation determine lower MP
- *Trans* configuration and conjugation of FAME with identical C-atoms and unsaturation are leading to higher melting points
- Branching of alkyl chain is decreasing the MP
- The alcohol chain is influencing the MP: methyl>ethyl>iso-propyl.

In this way, the MP of the FAAE is highly influencing the physical properties (CP, CFPP and viscosity) of biodiesel. The CP is higher for longer alkyl chains,
unsaturation is leading to lower CP and *trans* and conjugated esters have higher CP. Similarly, the kinematic viscosity of biodiesel is also influenced. In addition, substituents in the FAAE are leading to substantial higher viscosity. Dimeric fatty acids also produce biodiesel with a higher viscosity.

Physical properties of individual FAAE and of biodiesel from various feedstocks are given in Table 5.5 and Table 5.6. The oxidative stability is mainly influenced by the degree of unsaturation, with allylic and *cis*-allylic position more easily oxidized.

Other factors are the presence of natural anti-oxidants. Purification of biodiesel by distillation is decreasing the oxidative stability as a part of tocopherols remain in the distillation residue. The presence of hydroperoxides, metals (FE and Cu) and pro-oxidants (e.g. chlorophylls) cause a lower oxidative stability. In relation to physical properties of biodiesel, there is a conflict between saturation and unsaturation. Biodiesel produced from more saturated feedstocks has a higher CN and a better stability. However, the cold properties are negatively influenced by a high degree of saturation. It has been observed that sedimentation of insoluble

Fatty acid	Ester	Cetane number (CN)	Viscosity, mm²/sec	Melting point (MP), °C
CI2:0	ME	61.4	2.4	-
CIEO		51.2 74 5 (95 0)	4.4	20 F
C10.0	EE	(93.1)	4.4	30.5
CI8:0	ME EE	86.9 (101.0) 76.8 (101.0)	5.8	39.0
CI8:1	ME	47.2 (59.3) 53.9 (67.8)	5.8	-20.0
Cl8:2	ME EE	28.5 (38.2) 37.1 (39.6)	3.6	-35.0

Table 5.5 Physical properties of individual fatty acid alkyl esters

ME=ethyl esters EE=ethyl esters

Table 5.6	Physical	properties	of biodiesel	from	various	feedstocks
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Biodiesel	Cetane number (CN)	Viscosity, mm²/sec	Cold point (CP), °C
Rapeseed oil ME	55	3.8	-2
Soybean oil ME	49	4.1	2
Sunflower oil ME	47	4.2	0
Palm oil ME	56	4.1	13–15
Tallow ME	60	4.1	17

contaminants in biodiesel prepared from soy and palm oil might occur well above CP (Van Hoed, 2010).

### 5.7.2 Influence of the technology and processing

Pre-treatment of the feedstocks and the reaction conditions for the transesterification are influencing a number of biodiesel parameters such as ester content, acid number, glycerides content, glycerol content, total contaminations, metal content, ash and phosphorus.

The ester content is decreased by the presence of water in the feedstock, reactor and/or catalyst causing deactivation of the catalyst. Presence of FFAs can give rise to soap formation resulting in inadequate transesterification and poor layer separation due to emulsion formation. Poor catalyst neutralization after the reaction is causing hydrolysis and soap formation. The ester yields can be upgraded by: (1) drying of the feedstocks for water removal and (2) removal of FFAs via neutralization, stripping, alcohol extraction, combined esterification and transesterification, and (3) post-purification by distillation, filtration or adsorption.

The acid number of the biodiesel is too high due to non-removal of FFAs by refining or acid esterification, hydrolysis of methy esters during washing due to the presence of catalyst, hydrolysis during storage, presence of mineral acids due to the poor layer separation in work-up and washing.

Too high concentrations of mono-, di- and triglycerides arise from inefficient transesterification due to deactivation of the catalyst due to the presence of water or FFA. Another reason is a back reaction in which the glycerol anion is reacting with the FAMEs at low methanol concentration, especially during evaporation of the methanol in alkaline conditions. The presence of monoglycerides gives various problems. Monoglycerides are excellent emulsifiers leading to poor layer separation that results in high water, glycerol concentration, high total ash and contaminants and higher viscosity. In addition monoglycerides are easily precipitated leading to high CP and cold soak test.

Metal/mineral/ash content can be high due to poor layer separation, washing with hard water or due to the inappropriate pre-treatment of the feedstocks. However, post-treatment (adsorption and distillation) can solve these problems. Phosphorus and sulfur content of biodiesel can also be too high due to the nature of the feedstocks or the lack of efficient refining or pre-treatment and needs to be controlled.

The oxidative stability can be maintained by the exclusion of air during processing and storage by adding synthetic anti-oxidants and by post-treatment by adsorption.

Biodiesel in accordance with the standards will be dependent upon used feedstocks (especially for the physical parameters), used technology/processing/ reaction conditions (particularly for the chemical parameters and purity) and post-treatment (which is leading to an improvement of the biodiesel quality but also to additional costs and adequate combination of feedstock processing).

#### 5.8 Conclusions and future trends

Biodiesel is a renewable alternative to substitute petrodiesel. It was expected that by 2010, 5.75% biofuels should be used of which the majority will be biodiesel. Petrodiesel can be substituted by maximum 20% biodiesel without modifications of the engine. In the EU, the majority of blending is in the range four to seven per cent. In order to reach the biodiesel standards, refined oils and fats are the most suitable feedstocks. However, this is creating a competition with the food and feed applications.

Therefore, there is an increase in attention for other resources which are not creating ethical problems. Biodiesel can be prepared from waste or used oils and fats and from resources which are not competing with the food applications. Non-edible feedstocks such as jatropha and other seed oils can be converted into biodiesel using conventional processes. Algae oil has also a great potential to be a widespread feedstock in the future.

At this moment, biodiesel is mainly produced on industrial scale by homogeneous catalyzed transesterification. The use of heterogeneous catalysis is however looking promising with the advantage of easier post-treatment of glycerol. However, only two plants are now in operation using alkaline heterogeneous catalysts.

Many trials have been performed on laboratory scale using enzymatic production of biodiesel, we refer the readers to Chapter 6 in which this topic has been covered in detail.

The advantage of this technique is that simultaneously FFAs and TAGs are converted into FAAE. However, no industrial applications using enzymes are available until now.

Various other modifications have been proposed either to facilitate the reaction or to avoid pre- and/or post-treatment. Processes using solvents, microwave techniques, microreactors and others are proposed but these are not operating at large scale. The majority of methanol utilized for biodiesel transesterification is produced via petrochemistry. In order to be completely renewable, ethanol can be used. Bio-butanol produced by fermentation is also looking very promising in order to produce a complete green and renewable biofuel (see Chapter 9 for more details).

At this moment, the boom in biodiesel production is stopped and the capacity is used only for 50% due to the high price for the feedstocks and the cut-in-tax directives. However, if 20% of the fuel should be renewable for 2020, biodiesel is one of the most promising options to fulfill this goal.

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Biochemical catalytic production of biodiesel

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**Abstract:** This chapter discusses the enzymatic production of biodiesel using lipase enzyme as a biocatalyst. It starts by highlighting the advantages and limitations of the enzymatic approach and includes a review on the effects of the source of lipase, type and quality of feedstock, type of acyl acceptor and temperature. The chapter then discusses importance of using the lipase in immobilized form and different immobilization techniques. A kinetic model that is developed from the mechanismic steps of enzymatic transesterification of triglyceride is also presented. The chapter concludes with an exploration of the future advances in enzymatic biodiesel production.

**Key words:** enzymatic biodiesel production, waste oil feedstock, immobilized lipase, kinetic model.

### 6.1 Introduction

With the inevitable depletion of the non-renewable resources of fossil fuels, and due to its favorable environmental features, biodiesel promises to be the favorable fuel of tomorrow. Biodiesel is formed from transesterification of vegetable oils or animal fats with methanol (or ethanol) in the presence of a catalyst, as shown in Fig. 6.1. It is a renewable energy source that is non-toxic and biodegradable. Compared to petroleum-based diesel, biodiesel has lower emission levels of carbon monoxide, particulate matter and unburned hydrocarbons (Yusaf et al., 2005). In addition, using biodiesel on large scale will promote plantations of crops used to produce its feedstock, which results in more carbon dioxide recycling, minimizing its impact on the greenhouse effect (Korbitz, 1999; Agarwal and Das, 2001). Furthermore, biodiesel has a relatively high flash point (150°C) that makes it less volatile and safer to transport or handle than petroleum diesel (Krawcsyk, 1996). It provides lubricating properties, which reduce engine wear and extend engine life (Von Wedel, 1999). At the same time, biodiesel has physical properties and energetic content close to those of petroleum diesel, which allows its efficient function in conventional diesel engines without any modification.

The transesterification of triglycerides, being from vegetable oil or animal fat, is conventionally catalyzed chemically by alkaline or acid catalysts. The basic catalysts employed are sodium or potassium hydroxide because they are relatively inexpensive (Freedman *et al.*, 1984; Akoh and Swanson, 1988). Usually, a stoichiometric excess of methanol, in a molar ratio of 6:1 (methanol:vegetable oil), is preferred to increase methyl ester yield, and the reaction can be completed in a few hours at 40–65°C. The alkali-catalyzed processes, however, are sensitive



6.1 Transesterification reaction of triglycerides.

to moisture and free fatty acids (FFA) content in feedstock. Saponification reaction of the FFA consumes the alkali catalyst and at the same time generates soaps that cause the formation of emulsions, which increase the viscosity and create difficulties in downstream recovery and purification of the biodiesel. Therefore, pre-treatment of the oil is required for commercially viable alkalicatalyzed systems. This requirement is likely to be a significant limitation to the use of low-cost feedstock, and the cost of the highly refined feedstock can account to up to 70-80% of the final cost of the biodiesel (Fukuda et al., 2001). On the other hand, the acid-catalyzed processes are insensitive towards FFA contents. However, they are rarely used because they result in much slower reactions and produce by-products, from alcohol etherification, that also results in difficulties in downstream recovery and purification. In addition, careful removal of catalyst from the biodiesel fuel is essential, since acid-catalyst residues can damage engine parts (Fukuda et al., 2001). Furthermore, acid-catalyzed reactions require higher temperatures of around 55-80°C and higher substrate molar ratios of alcohol of around 30:1 to yield approximately 99% biodiesel in 50 h (Marchetti et al., 2007). The preferred acid catalysts are sulfuric, hydrochloric and sulfonic acids (Freedman et al., 1984).

Biodiesel can also be produced in the absence of any catalyst, using supercritical methanol (Demirbas, 2002). This simple process results in high yield due to the simultaneous transesterification of triacylglycerols and esterification of fatty acids. However, this is an energy intensive process that requires operating at temperatures and pressures above the critical points for methanol, which are 512 K and 8.1 MPa, respectively. Furthermore, operating at these harsh conditions destroys the antioxidant inherently found in the feedstock, which results in reducing the oxidative stability of biodiesel.

Recently, a less energy intensive and environmental friendly procedure has been proposed by using enzymes to catalyze the transesterification of triglycerides. Enzymatic transesterification can overcome the problems facing conventional chemical methods without compromising their advantages. Biodiesel has been successfully produced in lab scale by lipase-catalyzed reactions. Conversions as high as 90% have been reached within short reaction times, provided that the reaction takes place under the appropriate conditions. Nevertheless, there are many obstacles hindering the effective use of enzymes for commercial production of biodiesel in large scales. The most important challenges and the proposed ways to overcome them are presented in this chapter. In the following Section 6.2, a general introduction to the enzymatic approach is provided. The advantages of the enzymatic catalyzed process over conventional chemically catalyzed ones are also explained in this section. On the other hand, the limitations of enzymatic approach are presented in Section 6.3. In Section 6.4, the effectiveness of lipase, the enzyme to be used in biodiesel production, from different sources is discussed. After that the capacity of lipase to produce biodiesel from various feedstock, with special emphasis on feedstock that does not compete with food stock, is assessed in Section 6.5. This is followed by Section 6.6 that describes the effects of the type and amount of the acyl-acceptor on the enzymatic biodiesel production process and possible ways to overcome the inhibition by short-chain alcohols. In Section 6.7, the thermo-stability and optimum temperatures of lipases from different sources are presented. Section 6.8 discusses the use of immobilized lipase in biodiesel production. This is crucial since the cost of lipase remains the main obstacle facing full exploitation of its potential, the reuse of lipase is essential from the economic point of view, which can be achieved by using the lipase in immobilized form. In Section 6.9, the development of a kinetic model to describe the system, taking into consideration the inhibition effects by both substrates is presented. This chapter concludes with an explanation of the future advances in enzymatic biodiesel production and sources for further information in Sections 6.10 and 6.11, respectively.

### 6.2 The enzymatic process

Enzymes are proteins that work as nature's catalysts. They are specific in the reactions they catalyze and are very proficient in doing so. Enzymes consist of active sites where the substrates bind, in a favorable position and angle, and react. They lower the activation energies of reactions by large factors and, similar to mineral catalysts, they are not consumed in the process.

Typically, enzymes are named and classified according to the substrates they catalyze, or a word or phrase describing their activity. Accordingly, lipase would be the class of enzymes that hydrolyze triglycerides (or lipids) to produce fatty acids. However, lipases have also been found to display catalytic activity towards a large variety of alcohols and acids in ester synthesis reactions. Since the synthesis of methyl esters are of primary interest, lipase would be the appropriate enzyme to be used for biodiesel production. Lipase-catalyzed production of biodiesel has been proposed to overcome the drawbacks facing the conventional chemically catalyzed methods, and have shown promising results. Most importantly, glycerol can be easily recovered without any complex process, FFA contained in the oils can be completely converted to methyl esters and subsequent wastewater treatment is not required (Al-Zuhair, 2008). As shown in Fig. 6.2, the enzymatic process is less complicated and does not require as many upstream and downstream



6.2 Comparison between alkali (a) and enzymatic (b) processes.

operations, compared to conventional alkali-catalyzed processes. Furthermore, lipase-catalyzed transesterification is performed at low temperature and ambient pressure making it not only less energy intensive but also safer than chemically catalyzed reactions.

# 6.3 Limitations of the enzymatic approach

The method of production of biodiesel using lipase as catalyst has not yet been implemented in industrial scale due to certain constrains like high cost of enzyme, exhaustion of enzyme activity and enzyme inhibition by methanol. Enzymes such as proteases and carbohydrases have been used industrially for a number of years and corner the largest share of the worldwide enzyme market. While lipases at present account for less than 5% of the market, this share has the potential to increase dramatically via a wide range of different applications. The higher production costs of industrial lipase as compared with proteases and carbohydrases seem to be the main obstacle that hampers its wider industrial application. In order to overcome this limitation, lipase has to be repeatedly used, which is achieved by using it in immobilized form. Details of incentives of lipase immobilization are explained in Section 6.8.1. However, when lipase is used in immobilized form, another problem arises. The deposit of the by-product glycerol coating the immobilized lipase is formed during the process due to the low solubility of glycerol in biodiesel, which competitively inhibits the enzyme and reduces its activity by blocking the active sites (Dossat *et al.*, 1999; Du *et al.*, 2004; Al-Zuhair *et al.*, 2008).

Another hindrance of biodiesel production by lipase is the inhibition of the enzyme by methanol. The effect of alcohol, specifically methanol, on the enzymatic production of biodiesel has been thoroughly discussed in literature. While it is a reactant, it also inhibits the enzyme. It has been found that biodiesel production increases with increasing methanol concentration up to oil to methanol ratio of 3:1 and then decreases when methanol concentration is further increased (Shimada et al., 1999; Al-Zuhair et al., 2007; Al-Zuhair et al., 2008). This was also found by Noureddini et al (2005), although the ratio was higher (7.5:1). In general, it is widely accepted that methanol which is completely dissolved in the substrate mixture does not inactivate the lipases (Shimada et al., 1999; Shimada et al., 2002; Al-Zuhair et al., 2007). Lipases, however, are inactivated by contact with insoluble methanol that exists as drops in the oil; thereby the catalytic activity of the transesterification reaction is decreased. The deactivation of lipase with contact with insoluble methanol is due to the strong polarity of the latter, which tends to strip the active water from the active sites of the enzyme (Lara and Park, 2004). The inhibitory effect of methanol is large at the beginning of the reaction, but with increasing oil conversion it decreases because it is consumed in the reaction and hence its concentration decreases, in addition its solubility is higher in the product methyl ester than in the triglyceride (Shimada et al., 1999). On the other hand, the inhibition due to the blocking of the active sites of the catalyst by glycerol is absent at the beginning of the reaction and becomes larger at higher oil conversions.

Lipase is also sensitive towards the water contents. It has been reported that up to 500 ppm water in reaction mixture decreased the rate of methanolysis; however the equilibrium of the reaction was not affected (Shimada *et al.*, 1999). The effect of water content on the production of biodiesel from soybean oil using lipases from *R. Oryzae* (Kaieda *et al.*, 1999), *C. rugosa* and *P. Fluorescens* (Kaieda *et al.*, 2001), Novozym 435 (Shimada *et al.*, 1999) and *Burkholderia cepacia* (Noureddini

et al., 2005) have all shown that enzyme activity was low in absence of water; with the addition of water a considerable increase in lipase activity was observed, which is explained by the unique property of interfacial activation of lipase (Verger et al., 1973; Brady et al., 1990). The activity of lipases is low in monomeric solutions of lipid substrates but a configuration change and activity enhances strongly at the water-lipid interface. Activation of the enzyme involves unmasking and restructuring of the active site through conformational changes of the lipase molecule, which requires the presence of oil-water interface. An experimental approach to determine the activation of the lipase at the interface, proposed by Rooney and Weartherley (2001), was used by Al-Zuhair et al. (2003) to determine that the activity of lipase from C. rugusa at the oil interface, and was found to be 15.7% higher than that in the bulk. With the increased addition of water, the amount of water available for oil to form oil-water droplets increases, thereby, increasing the available interfacial area. However, excess water stimulates the competing hydrolysis reaction, since lipases usually catalyze hydrolysis in aqueous media. The optimum water content is a compromise between minimizing hydrolysis and maximizing enzyme activity for the transesterification reaction. The range of water content at which the enzyme maintains its methanolysis activity varies significantly from one type of lipase to another. For example, the activity of Novozym 435 significantly drops at water contents higher than only 0.1% (Shimada et al., 1999), whereas lipase from R. meihei maintains its methanolysis activity at water contents of up to 20% (Al-Zuhair et al., 2006; Tweddell et al., 1998).

# 6.4 Sources of the enzyme: lipase

Lipases are classified according to the sources from which they are obtained, such as microorganism, animal and plant. Lipase can easily be produced in high yields, by fermentation processes and few basic purification steps, from microorganisms such as fungi (e.g., Candida antarctica) or bacteria (e.g., Pseudomonas fluorescens). Lipases from animal or plant sources are rarely used in industry, and hence, the focus of this section will be on lipases from microbial sources, which have real industrial potential. Some lipases show position specificity towards the substrate, whereas others do not. Pure lipases extracted from different sources have been successfully used in the production of biodiesel; however, Candida antarctica B lipase, immobilized on acrylic resin, commercially known as Novozym 435, has been by far the most commonly used enzyme for the production of biodiesel. A comparative study on the type of free lipases from different sources revealed that P. fluorescens lipase has the highest enzymatic activity (Iso et al., 2001; Kaieda et al., 2001). Generally, lipases from fungal sources show better transesterification activity of triglycerides compared to those from bacterial sources (Al-Zuhair et al., 2008). Table 6.1 shows examples of lipases from different sources previously used in biodiesel production.

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Lipase	Oil	Acyl acceptor	Optimum temperature	Reference
Novozym 435 Novozym 435 Novozym 435 Novozym 435 Novozym 435	Soybean oil Soybean oil Canola oil Rice bran oil Olive oil	Methanol Methyl acetate Methanol Methanol Methanol	8°C 0°C	Kaeida <i>et al.</i> (2001) Wei <i>et al.</i> (2004) Chang <i>et al.</i> (2005) Lai <i>et al.</i> (2005) Sanchez and Vasudevan
Novozym 435 Novozym 435	Vegetable oil Waste ABE	Methanol Methanol, ethanol, 1-propanol, 1-butanol, iso-butanol, iso-amylalcohol, and <i>n</i> -octanol		(2006) Shimada <i>et al.</i> (2002) Lara and Park (2004)
R. delemar R. miehei R. miehei C. rugosa	Vegetable oil Vegetable oil Palm oil Waste ABE	Methanol Methanol Methanol, ethanol, 1-propanol, 1-butanol, iso-butanol, iso-butanol, and <i>n</i> -octanol		Shimada <i>et al.</i> (2002) Shimada <i>et al.</i> (2002) Al-Zuhair <i>et al.</i> (2007) Lara and Park (2004)
C. rugosa C. antarctica C. lipolytica C. lipolytica K. oxytoca P. camembertii P. fluorescens P. fluorescens P. fluorescens P. cepacia P. cepacia P. cepacia	Jatropha oil Waste oil Soybean oil Soybean oil Soybean oil Soybean oil Triolein Jatropha oil Soybean oil Jatropha oil Waste oil	Ethanol Methanol Methanol Methanol Methanol Methanol 1-Propanol Ethanol Methanol Ethanol Methanol	0°C 0°C	Shah and Gupta (2006) Al-Zuhair <i>et al.</i> (2008) Kaieda <i>et al.</i> (2001) Kaieda <i>et al.</i> (2001) Kaieda <i>et al.</i> (2001) Kaieda <i>et al.</i> (2001) Iso <i>et al.</i> (2001) Shah and Gupta (2006) Kaieda <i>et al.</i> (2001) Shah and Gupta (2006) Al-Zuhair <i>et al.</i> (2008)

#### Table 6.1 Microbial lipases used for the production of biodiesel

### 6.5 Feedstock

### 6.5.1 Straight plant derived oil

Plant-derived oils are considered a good substitute raw material for diesel energy supply because they are carbon dioxide neutral. The term 'carbon neutral' refers to the balance between the  $CO_2$  released by combustion of plant-derived fuel and that utilized during the green plants growth through the photosynthesis process. Several types of vegetable oils can be used for the preparation of biodiesel, as shown in Table 6.1. The source of oil crops will depend on their availability and varies by

regions. Nevertheless, viable crops most importantly must be cheap, of high production yield per hectare and have to be rich in oil content (Pinto *et al.*, 2005). Palm oil is leading the gains in vegetable oil production worldwide and has the highest yield per hectare, estimated at  $5.95 \text{ m}^3$  per hectare (Chisti, 2007) compared to, for example, soybean oil production yield of only 0.45 m<sup>3</sup> per hectare. Therefore, it would be economically intuitive to consider palm oil as a preferable feedstock for biodiesel production; although there are no technical restrictions to the use of any other type of vegetable oils. On the other hand, high oleic acid containing oils are preferred because of the improved fuel properties and increased stability of their alkyl esters on storage (Pinto *et al.*, 2005). In that regard, soybean, palm kernel, cottonseed, sunflower, and castor bean oils are the more favorable.

#### 6.5.2 Waste oils and fats

Utilizing any type of unused plant-derived oils, also known as straight oil (SO), as feedstock is economically infeasible, resulting in a high final cost of the biodiesel. Above that, it raises ethical questions as this feedstock competes with food stock. Shah and Gupta (2006) argued that it is more reasonable to use inedible oils such as Jatropha oil. This argument however is debatable, as a land has to be developed for plantation, and it would be more advisable then to use it to plant something that can be used as food stock. The only sensible way to overcome this dilemma is to use waste oils (WO) and waste fats (WF) as raw materials for biodiesel production. In addition to using feedstock that does not compete with food stock in this case, the use of WO and WF is considered an important waste minimization and recycling process, no less than half a million tons of which are discarded every year in Japan alone (Kaieda *et al.*, 1999).

In comparison to SO, WO has significantly higher amounts of water, around 2000 ppm and FFA, 10-15% (Zhang et al., 2003; Lai et al., 2005), as well as higher polymerization products. As explained earlier, the high FFA content renders alkalicatalysts processes not suitable, and the use of chemical catalysts is limited in this case to the acidic ones (Zhang et al., 2003). Due to the comprehensible attractive benefits of WO, biodiesel production from this feedstock has been investigated using acidic catalysts, despite being much slower and more hazardous catalysts compared to the other chemical catalyst, namely the alkaline (Al-Widyan and Al-Shyoukh, 2002; Al-Widyan et al., 2002; Zhang et al., 2003). Methanolysis of triacylglycerols (TAGs) with a lipase is considered one of the effective reactions for production of biodiesel fuel from WO. Shimada et al. (2002) have successfully produced biodiesel from WO using immobilized lipase from C. antarctica. They have further proved that the yield of biodiesel production from WO, containing up to 2000 ppm water, was comparative to that from SO. WO containing around 500 ppm water was also successfully utilized to produce biodiesel, using lipase from bacterial, P. cepacia, and yeast, C. antarctica, sources in free and immobilized on ceramic beads forms, in the presence and absence of *n*-hexane (Al-Zuhair et al., 2008).

Animal fats have also been used for biodiesel production (Ali *et al.*, 1995). However, due to the high melting point of animal fats, that is usually near the denaturation temperature of lipase, and because methanol and animal fat are immiscible, the reaction system has to take place in an organic solvent to dissolve the solid fat (Ma *et al.*, 1999). The use of organic solvent, however, requires the addition of solvent recovery unit. To overcome this drawback, thermostable lipases, which have relatively high optimum temperature, can be used.

### 6.5.3 Microalgal oil

Cellular biomass of oleaginous yeasts and filaments fungi (Miao and Wu, 2006) has also been evaluated as a cheap source of renewable raw materials for biodiesel production. In addition to being cheap, using microalgae to produce biodiesel will not compromise production of food and other products derived from crops. Above that, oil crops, waste cooking oil and animal fat cannot realistically satisfy the demand required to achieve the target of replacing all current transport fuel consumed with biodiesel. This scenario changes dramatically, if microalgae are used to produce biodiesel. It has been reported that for microalgae of 30% oil content per weight of biomass, the oil yield per hectare is estimated at 58.7 m<sup>3</sup> per hectare (Chisti, 2007). This is almost ten times the yield of palm oil, and the difference becomes even higher if compared to microalgae of 70% oil content per weight of biomass. It appears therefore that microalgae are the only source of biodiesel that has the potential to completely displace fossil diesel. Microalgae commonly double their biomass within 24 h. However, during exponential growth period, doubling times are as short as 3.5 h (Chisti, 2007). In addition, oil content in microalgae may exceed 80% by weight of dry biomass (Spolaore et al., 2006).

Besides microalgae, other oil producing heterotrophic oleaginous microorganisms have been used to produce biodiesel (Ratledge and Wynn, 2002). Nevertheless, heterotrophic production is not as efficient as using photosynthetic microalgae, because the renewable organic carbon sources required for growing heterotrophic microorganisms are produced ultimately by photosynthesis, usually in crop plants, which brings us back to square one.

The use of oils from microalga, *Chlorella protothecoids* for large-scale biodiesel production using immobilized *Candida* sp. lipase has been reported (Li *et al.*, 2007). Algal oils have been largely produced through substrate feeding and heterotrophic fermentation. In their work, Li *et al.* (2007) achieved an increase in the lipid content up to 48% of the cell dry weight of the microalga. The oils were then used as raw material to produce biodiesel using immobilized *Candida* sp. lipase.

### 6.6 Acyl acceptors

Methanol is the most commonly used alcohol in biodiesel production, as shown in Table 6.1, mainly because of its high reactivity and relatively low cost. However, sustainable methods of methanol production are currently not economically viable. It is typically produced from syngas that is in turn produced from a non-renewable source, namely natural gas. In addition, methanol is the most toxic and has the most deleterious effect on the biocatalyst activity compared to other alcohols. On the other hand, ethanol can be easily formed from renewable sources by fermentation. Using ethanol that is produced from renewable resources for biodiesel production makes the process entirely 'green'.

The reason lipase-based biodiesel production has not reached commercial potential at present is the high cost of the enzyme and the loss of its activity. The main reason for the loss of activity is due to the inhibition effect of alcohol. As mentioned in Section 6.3, lipases are inactivated by contact with insoluble methanol that exists as drops in the oil, due to the strong polarity of the methanol that strips the active water from the enzyme's active site (Lara and Park, 2004). Another potential problem that arises with the use of lipases is the by-product glycerol inhibition of the lipase due to its strong adsorption onto its surface. To overcome the problem of methanol inhibition of lipase, its amount should always be kept below its solubility limits in oil. To achieve this efficiently, a stepwise addition of methanol in a way to keep its amount below its solubility limit has been proposed (Shimada *et al.*, 1999; Shimada *et al.*, 2002). However, this solution does not take into account the problems with glycerol inhibition.

Other ways to overcome the problem include the use of an organic solvent, which are mainly used to dissolve the methanol and eliminate the stripping of the water molecules required for enzyme activation. The use of organic solvents also helps to reduce the effect of the by-product inhibition by dissolving the produced glycerol and to reduce the viscosity of the reaction media. Organic solvents such as *n*-hexane and ether have been studied (Tweddell *et al.*, 1998; Oliveira and Oliveira, 2001; Al-Zuhair et al., 2008); however the solubility of methanol and glycerol in these solvents is low, and the above problems probably persist. Since the solubility of methanol is higher in 1,4-dioxane, using it as a solvent results in an increased yield of biodiesel production from triolein (Iso et al., 2001). However, large amounts of this solvent that make up 90% of reaction media were required to obtain reasonable conversion. The main disadvantages of using organic solvents are substrate dilution and the requirement of the addition of solvent recovery unit. On the other hand, it was found that when using t-butanol, a long-chain alcohol that does not inhibit the enzyme, as a solvent the enzymatic process is improved (Wang et al., 2006; Royon et al., 2007). t-Butanol dissolves both methanol and glycerol and at the same time it is not a preferred substrate for lipase that does not act as tertiary alcohols. The advantages of using t-butanol with immobilized lipase is further discussed in Section 6.8.

An alternative approach is to replace methanol with a different acyl acceptor such as methyl acetate (Wei *et al.*, 2004). The reaction of triglyceride with methyl acetate is known as interesterification, which is similar to transesterification with the main difference being that the main by-product is triacetyl-glycerol rather than

glycerol. Unlike methanol, methyl acetate has no negative effect on enzymatic activity and almost no loss in lipase activity detected even after being continuously used for 100 batches (Du *et al.*, 2004; Wei *et al.*, 2004). However, the main disadvantage of this approach is that it proceeds in a much slower rate compared to when methanol is used in appropriate concentrations (Wei *et al.*, 2004). In addition, the removal of the by-product tri-acetyl-glycerol is more difficult than glycerol.

Ionic liquids, which are salts that are liquid at room temperature, have also been proposed to replace conventional organic solvents often with improved process performance. Ha *et al.* (2007) assessed the effectiveness of using several types of ionic liquids in a lipase-catalyzed production of biodiesel from soybean oil and methanol. They reported that higher percent conversions were achieved using hydrophobic ionic liquids as compared to solvent-free systems. The cost of these ionic liquids is expected to hinder their commercial application.

# 6.7 Effect of temperature

The increase in temperature of a reaction mixture usually results in an increase in the reaction rate. This is mainly due to the increase in rate constants with temperature and partly due to the reduction in viscosity and mass transfer resistances. However, in enzymatic catalyzed reaction, this increase in reaction rate with temperature persists up to a certain optimum temperature, after which the rate decreases sharply. This sharp drop takes place at the onset of the denaturation of the enzyme that occurs at elevated temperatures. In addition to the deactivation of the enzyme, the presence of the inactive enzyme at the interface blocks the active enzyme from penetrating the interface, which would further decrease the reaction rate. This trend has been consistently observed in all studies that investigated the effect of temperature on the production of biodiesel by lipase. The critical temperature, at which the enzyme starts to deactivate, was different as shown in Table 6.1. Generally, lipases from bacterial sources, such as those from Pseudomonas species, have relatively higher thermo-stability than lipases from yeast source, such as those from Candida species that include Novozym 435. For example, the optimum operating temperature of lipase from P. fluorescens has been reported to be 65°C (Fukuda et al., 2001), whereas that of lipase from Novozym 435 has been reported to be 35-40°C (Chang et al., 2005). Immobilization provides a more rigid external backbone for lipase molecule, allowing it to maintain its activity at higher temperatures than if it is in free-form. Hence, the reaction optimum temperature is expected to increase, which results in faster rate of reaction.

# 6.8 Immobilized lipase

The practical use of free lipase in reaction systems suffers from technological difficulties such as contamination of the products with residual enzymatic activity and economic difficulties such as the use of enzyme for a single reactor pass.

Hence, part of the overall potential enzymatic activity is lost. If the lipase is immobilized, it becomes an independent phase within the reaction system, which may easily be retained in the reactor with concomitant advantages of preventing contamination of the products and extending its useful active life. Furthermore, as mentioned in Section 6.7, immobilization provides a more rigid external backbone for lipase molecule, allowing it to maintain its activity at higher temperatures than if it is in free-form. Therefore, the reaction optimum temperature is expected to increase, which results in faster rate of reaction. In addition, immobilization of lipases has been proposed as a countermeasure to the high water content usually present in WO (Fukuda *et al.*, 2001). Furthermore, by immobilization, the enzyme is dispersed over a large surface, which results in an enhanced catalytic performance, especially in organic media, which is the case in biodiesel production. It was shown that lipase from *C. antarctica* performed better when immobilized on ceramic beads than in free-form (Al-Zuhair *et al.*, 2008). Similar results were also found using lipase from *P. cepacia* (Shah and Gupta, 2006).

The main advantage of immobilization of lipase, however, is the ability of repeated use. The ability to use the immobilized enzyme repeatedly is actually the factor that determines its effectiveness. Due to the negative effect caused by by-product glycerol adsorption on the surface of the immobilized lipase, a loss in activity is inevitable with repeated uses. However, the immobilized lipase retained more than 70% of its initial activity even after more than ten cycles. This was found when using different lipases immobilized on different solid surfaces, such as Novozym 435 (Wei et al., 2004) and P. fluorescens lipase immobilized on toyonite (Iso et al., 2001). Organic solvents are usually used to dissolve the by-product glycerol, which clogs the active sites of the immobilized lipase. By using t-butanol as solvent, Wang et al. (2006) showed that there is no obvious loss in biodiesel yield even after immobilized lipase from T. Lanuginosa was used for 120 cycles. Even better results were found by Li et al (2006) using immobilized lipase from T. Lanuginosa and Novozyme 435; with the number of cycles reaching 200. However, as mentioned earlier, the addition of organic solvent has inherent problems, such as, diluting substrates and requiring additional solvent recovery unit.

From an economical point of view, a continuous reaction process without the use of any organic solvent is needed for the industrial production of biodiesel. It has been shown that the activity of immobilized lipase could be significantly increased and deactivated enzyme could be regenerated when *t*-butanol was used for an immersion pretreatment of the enzyme (Chen and Wu, 2003). It was shown that the activity of pretreated Novozyme 435 increased about tenfold in comparison to the enzyme not subjected to pretreatment. In addition, following complete deactivation by methanol, washing the enzyme with *t*-butanol successfully regenerated the enzyme and restored up to 75% of its original activity level. Recently, it was found that activity, methanol tolerance and operational stability of immobilized lipase from *Candida* sp. 99-125 can be significantly enhanced by pretreatment with 1 mM salts solutions of CaCl<sub>2</sub> and MgCl<sub>2</sub> (Lu *et al.*, 2010). The reason might be that these

salts incorporate with the protein to form a more stable molecule that resists conformational change induced by high methanol concentration.

### 6.8.1 Lipase immobilization by adsorption

Among all immobilization methods, physical adsorption has been elected by most researchers due to its ease, absence of expensive and toxic chemicals, ability to retain the activity and feasibility of regeneration. On the other hand, poor adsorption of the enzyme results in its leaching off the support surface, which favors other means of enzyme immobilization such as covalent bonding, entrapment and encapsulation. It is possible to strengthen the attachment between the water-soluble enzyme and the water-insoluble surfaces by using multifunctional agents that are bifunctional in nature and have low molecular weight, such as glutaraldehyde (Shamel *et al.*, 2005; Shamel *et al.*, 2007). Nevertheless, physical adsorption remains the most attractive method industrially, because of its simplicity and economical effectiveness.

It has been shown that the adsorption of lipases from *M. miehei* on porous polysulfone surface (Shamel *et al.*, 2005) and on modified regenerated cellulose hollow fiber membranes (Shamel *et al.*, 2007) can be described by the Langmuir isotherm (Eq. [6.1]), which relates the amount of adsorbed lipase activity,  $a_{ads}$ , to that present in the supernatant solution,  $a_{free}$ , at equilibrium.

$$a_{\rm ads} = \frac{a_{\rm ads,max} K_{\rm ads} a_{\rm free}}{1 + K_{\rm ads} a_{\rm free}}$$
[6.1]

A convenient way to express the temperature-dependent parameters  $K_{\rm ads}$  and  $a_{\rm ads,max}$  takes advantage of Van't Hoff's relationship between the equilibrium constant and the standard enthalpy change associated with the process under consideration:

$$K_{\rm ads} = \beta \exp\left(\frac{-\Delta h_{\rm ads}}{RT}\right),$$
[6.2]

$$a_{\text{ads,max}} = \alpha \ (1 + \varepsilon T). \tag{6.3}$$

Experimental results showed that, unlike the general behavior of physical adsorption, increasing the temperature results in an increase in the equilibrium amount of enzyme adsorbed on both surfaces. This was a result of the increase in the diffusion of lipase into the micropores due to expansion of the pores and the reduction of the solution viscosity at higher temperatures.

### 6.8.2 Other immobilization techniques

Beside the adsorption technique, lipase can be immobilized on support surfaces by covalent anchorage, electrostatic binding and entrapment within inorganic or organic

inert matrices. Adsorption techniques are simple, but the binding forces between the enzyme and the support are weak and enzyme leaching often occurs. A higher degree of stability can be achieved by covalent bonding between the enzyme and the solid surface (Shamel et al., 2005; Shamel et al., 2007); however this requires several chemical steps that are accompanied by loss in enzyme activity. High stability can also be achieved by electrostatic interaction, but this technique is limited to be used at pH values compatible with the electrostatic point, which also may affect the activity of the enzyme, since the enzyme conformation changes as function of pH (Macario et al., 2007). On the other hand, the immobilized lipase by entrapment within a polymer matrix is much more stable than physically adsorbed lipase (Hartmeier, 1985), and unlike the covalent bonding this method uses a relatively simple procedure. Enzyme entrapment in a silica matrix by sol-gel offers a good compromise between stability of the heterogeneous biocatalyst and activity loss, and hence this technique has received considerable attention in recent years (Frings et al., 1999). Entrapment of lipase in an inorganic polymer matrix, which is based on sol-gel process, is well documented (Reetz, 1997). The method involves an aqueous solution of the enzyme, an acid or base (NaOH, NaF or HCl) as catalyst and an alkoxysilanes as inorganicorganic matrix precursor. The sol-gel material is then obtained by hydrolysis and condensation of the precursor to result in an amorphous silica matrix that entraps the enzyme. The lipase entrapped in sol-gel has been used for biodiesel production (Orcaire et al., 2006; Al-Zuhair et al., 2008) and was easily recovered from reaction media. However, under the same operating conditions, it was found that immobilized lipases, from P. cepacia, on ceramic beads were more capable of transesterifying WO of high water contents to biodiesel than lipase, from the same course, entrapped in sol-gel matrix (Al-Zuhair et al., 2008), which is mainly due to diffusional limitations.

Covalently immobilized lipases are usually prepared in almost anhydrous media. This usually results in a problem, especially in porous structures, which is mainly used to enhance the interfacial area. At the oil water interface, lipases are in open active form, where a flap (or lid) that would seclude the active cites is moved to allow substrate accessibility to the active sites (Verger et al., 1973; Brady et al., 1990). When inside a porous structure, lipase molecules become inaccessible to external surfaces, which prevent their activation. Therefore, it has been proposed to use hydrophobic support that resembles the surface of drops of the natural substrates to immobilize lipase on. In this case, the adsorbed lipases are in open form, with the active sites accessible for substrate and the immobilized enzyme in this case exhibit significantly enhanced activity (Bastida et al., 1998). Based on that Palomo et al. (2002) used an epoxy acrylic matrix, Sepabeads, with the surface covered by octadecyl groups, yielding a very hydrophobic surface that has large pores to allow intensive protein interaction. The support permits in one step immobilization, purification, hyper-activation and stabilization of surface in a very simple protocol: the mere addition of support to the lipase solution at very low ionic strength. In addition, the support is rigid enough to be used in packedbed reactor and does not swell in any reaction media. The stability and activity of lipases from *C. antarctica*, *C. rugusa* and *M. miehei* immobilized on this support were found to be superior to other covalently attached derivatives.

#### 6.8.3 Immobilized whole cells

In order to reduce the cost of enzymatic production of biodiesel, the lipase producing whole cells rather than the isolated enzyme has been used. This eliminates the need for isolation and purification steps before immobilization, which results in a considerable reduction in the cost. Air drying immobilization technique of lipase producing *Rhizopus oryzae* whole cells was developed by Matsumoto *et al.* (2001). The use of immobilized whole cells to produce biodiesel by three stepwise addition of methanol in solvent-free system was reported to achieve biodiesel yield of 71% after 165 h.

Hama *et al.* (2004) found that the fatty acid composition affects the activity of the whole cells by influencing their membranes. It was reported that pretreatment of the whole cells with oleic acid and linoleic acid resulted in higher enzymatic activity, whereas palmitic acid pretreated cells showed higher stability. To compensate for both activity and stability, an optimum ratio of unsaturated to total fatty acids of 0.67 was proposed. Using the pretreated whole cells, methanolysis yields were consistently above 55% even after ten repeated cycles. To explain the fatty acids composition effect, Hama *et al.* (2006) suggested the existence of two types of lipases: one bound to the cell wall, which plays role in stability, and the other to the cell membrane, which plays role in methanolysis activity. The increase in enzyme activity with addition of unsaturated fatty acids was expected to be due to the increase in the production of membrane-bound lipase.

The immobilized lipase producing whole cells from R. oryzae were prepared in cuboidal polyurethane foam biomass support particles in a 20L air-lift batch cultivation bioreactor and used in a packed-bed reactor for continuous production of biodiesel by methanolysis of soybean oils (Hama et al., 2007). Compared with methanolysis reaction in a shaken bottle, the packed-bed reactor enhanced repeated batch methanolysis by protecting immobilized cells from physical damage and excess amounts of methanol. The flow rate of reaction mixture had to be optimized, as low flow rates resulted in a significant decrease in activity due to the covering of the immobilized whole cells with a hydrophilic layer of high methanol concentration, and high flow rates resulted in cells leaching. A highest biodiesel yield of 90% was achieved at a flow rate of 25 L h<sup>-1</sup>. The yield dropped to around 80% after the tenth cycle. To overcome the leaching problem, crosslinking treatment with 0.1% glutaraldehylde has been proposed (Ban et al., 2002). By glutaraldehyde treatment, biodiesel yield of 83% was maintained after six batch cycles in the stepwise methanol addition process, compared to only 50% without glutaraldehyde treatment.

Recently, Tamalampudi *et al.* (2008) used the same immobilized whole cells prepared by Hama *et al.* (2007) for the production of biodiesel from relatively low

cost, inedible oil from the seeds of *Jatropha curcas* in a 50ml screw-capped vessels with reciprocating shaking at 150 rpm. The activity of immobilized whole cell was compared with that of Novozym 435 and was found to be more efficient. The maximum biodiesel was 80% after 60 h using the former catalyst, whereas using the latter the maximum yield was only 76% after 90 h.

### 6.9 Kinetics of enzymatic production of biodiesel

Although the application of lipase in the production of biodiesel from vegetable oils has been thoroughly addressed in the literature, most of the studies were purely parametric. On the other hand, significant number of kinetic studies is found in the literature on the esterification of free fatty acids rather than the transesterification of vegetable oil. The industrial interest, however, is on the production of biodiesel from the triacylglyceride (oil), not the free fatty acids. The main difference between esterification of free fatty acids and transesterification of triglycerides (oils) is that in the first O-H bonds are broken, whereas in the second ester bonds are the ones that are broken. In addition, the by-product of esterification is water, whereas it is glycerol in transesterification. An attempt to model vegetable oil transesterification was done (Al-Zuhair, 2005), assuming that the reaction took place in two consecutive steps. In the first step, triglycerides are hydrolyzed to produce free fatty acids and in the second step, the free fatty acids produced in the first step are esterified to produce fatty acids methyl esters. This study combined the enzymatic kinetics models of hydrolysis of oils (Al-Zuhair et al., 2003) and esterification of FFA (Janssen et al., 1999; Krishna and Karanth, 2001). However, it was later shown that it was more accurate to assume that transesterification takes place by direct alcoholysis of the triglycerides (Al-Zuhair et al., 2007). In order to understand the reaction behavior and to propose suitable mechanismic steps, experimental determination of the separate effects of oil and methanol concentrations on the rate of enzymatic transesterification were determined. The proposed mechanism of alcoholysis of oils was based on the enzymatic hydrolysis mechanism (Bailey and Ollis, 1986) and presented by a Ping-Pong Bi Bi mechanism shown in Fig. 6.3. To account for the inhibition by alcohol, competitive inhibition was assumed when an alcohol molecule reacts with the enzyme directly to produce a dead-end enzyme-alcohol complex (E.A). And to account for the inhibition by the substrate, competitive inhibition was also assumed when a substrate molecule reacts with the acylated enzyme to produce another dead-end complex, namely, acylated enzyme-substrate complex (E-Ac.S). Based on this mechanism and assumptions, the reaction rate presented in Eq. [6.4] was derived:

$$\upsilon = \frac{V_{\text{max}}}{1 + \frac{K_{\text{IA}}}{[A]} \cdot \left[1 + \frac{[S]}{K_{\text{S}}}\right] + \frac{K_{\text{IS}}}{[S]} \cdot \left[1 + \frac{[A]}{K_{\text{A}}}\right]},$$
[6.4]



6.3 The mechanism of enzymatic production of FAME from triacylglycerides. A: alcohol, Bd: FAME (biodiesel), G: glycerol moiety, S: ester bond on the triglyceride (substrate) E.S: enzyme–substrate complex, E.Ac.G: acylated enzyme–glycerol moiety complex, and E. Ac.A: acylated enzyme–alcohol complex.

where v is the initial reaction rate,  $V_{\text{max}}$  is the maximum reaction rate,  $K_{\text{S}}$  and  $K_{\text{A}}$  are the dissociation constants for the substrate (S) and the alcohol (A), respectively, and  $K_{\text{IS}}$  and  $K_{\text{IA}}$  are the inhibition constants for the substrate and the alcohol, respectively. Numerical values of the parameters found in Eq. [6.4] are shown in Table 6.2 for lipases from different sources.

Equation [6.4] describes the initial reaction rate in the absence of any product inhibition, which is similar to the one proposed by Krishna and Karanth (2001) for the esterification of short-chain fatty acids with alcohol. On the other hand, Janssen *et al.* (1999) derived an equation to be used when the water, taken as one of the products, was assumed to inhibit the reaction. This modification was applicable when free fatty acids were considered as the substrate. However, when the substrate was the triglyceride, the product water is replaced with monoglyceride, diglyceride or glycerol. And unlike water which is usually present in the reaction medium at time zero, these products are not. Therefore, the product inhibition was neglected, especially when considering the initial rate of reaction.

Parameter	Using <i>M. meihei</i> lipase (Al-Zuhair <i>et al.,</i> 2007)	Using <i>C. antarctica</i> lipase (Al-Zuhair <i>et al.,</i> 2008)
$V_{\rm max}$ (mol m <sup>-3</sup> min <sup>-1</sup> )	0.041	1.96
$K_{\rm s}$ (mol m <sup>-3</sup> )	430	250
$K_{\Lambda}$ (mol m <sup>-3</sup> )	350	110
$\tilde{K_{us}}$ (mol m <sup>-3</sup> )	$4.45 \times 10^{4}$	$2.8 \times 10^{4}$
$K_{IA}$ (mol m <sup>-3</sup> )	$3.3 \times 10^4$	$3.5 \times 10^{4}$

Table 6.2 Comparison between the values of  $V_{\text{max}}$ ,  $K_{\text{S}}$ ,  $K_{\text{A}}$ ,  $K_{\text{IS}}$  and  $K_{\text{IA}}$ 

### 6.10 Future trends

### 6.10.1 Advanced bioreactor configurations

As explained earlier, the cost of lipase production is the main hurdle to the commercialization of the enzymatic process. Therefore, the reuse of lipase is essential from the economic point of view, which can be achieved by using the lipase in immobilized form. The operational stability of the catalyst in a continuous process plays a vital role. Further details about stability and possible ways of enhancing it is found in Sections 6.6 and 6.8. Shimada et al. (2002) achieved 93% conversion of SO in absence of organic solvents in a series of three continuous packed-bed bioreactors at a rate of 6.0 ml h<sup>-1</sup>. The productivity relative to the total mass of enzyme used was however lower than when t-butanol was added to the continuous reactor (Royon et al., 2007). The necessity of solvent recovery can be a drawback to such a process. However, the relatively low optimum *t*-butanol concentration, and low boiling point, allows easy separation, and hence the energy expense required for its recovery is usually acceptable. Chen and Wu (2003) achieved 70% conversion in continuous packed-bed bioreactor in the absence of organic solvent, but with periodical regeneration of the immobilized lipase with t-butanol washing. Nie et al. (2006) used lipase immobilized on cheap cotton fibers in a series of three packed-bed bioreactors with stepwise addition of methanol to produce biodiesel from SO and WO and achieved 93% and 92% conversions, respectively. A hydrocyclone was used on-line to separate glycerol. The operational stability of the immobilized lipase was more than 20 days at input flow rate of 15 L  $h^{-1}$  of substrate and ether solvent in a volume ratio of 2:3.

On the other hand, the use of membrane bioreactors for the enzymatic processing of fats and oils is increasingly becoming more attractive to substitute conventional stirred tanks or packed-bed reactors (Basheer et al., 1994). As the reaction proceeds, glycerol is generated and physically mixes with the alcohol to form a second liquid phase that is not completely miscible with the oil. This second polar organic phase serves to extract alcohol from the oil phase, thereby decreasing the concentration of this substrate in the reaction medium and causing a concomitant decrease in the conversion achieved in a fixed amount of time. In addition, glycerol is adsorbed on the surface of the immobilized lipase, and blocks the substrate from reaching the active sites. Consequently, conversions will be enhanced if glycerol is removed from the substrate mixture as the reaction proceeds. To achieve this, membrane reactors with immobilized lipase are proposed, which may take either a flat sheet (Isono *et al.*, 1998) or hollow fiber form (Hilal et al., 2004; Shamel et al., 2005). Membrane reactors enhance efficiencies by combining in one unit a reactor that generates a biodiesel and a separator that separates it from the other products. Removal of a product drives equilibrium-limited reactions towards completion and prevents product inhibition.

### 6.10.2 Genetic engineering

Current attention in lipase production is focused on genetic engineering as there is a hope that the cost can be reduced by gene technology such as gene amplification in addition to a traditional random mutation. The first and essential step of genetic manipulation is cloning of gene involved in the enzyme's biosynthesis. Recently, a gene of bacterial lipases and mammalian phospholipase A2 has been cloned. A number of genes of lipase will be cloned rapidly in the coming years. The use of recombinant DNA technology (genetic engineering) to produce large quantities of recombinant lipases will help lower the enzyme cost, which has been rendering the enzymatic approach of biodiesel production unattractive. In addition, protein-engineering approaches will help the elucidation of shortchain alcohol denaturation and will create novel enzyme proteins that are more resistant. Furthermore, the introduction of a new generation of cheap and highly thermo-stable enzymes should change the economic balance in favor of lipase use. Recombinant lipases with enhanced or altered activities and resilience towards short-chain alcohols can be mass produced after over-expression in relevant microorganisms, therefore making the overall process economically viable. In addition, genetic engineering can be used to improve fatty acid chain-length specificity, substrate specificity, alcohol chain length specificity, pH stability and productivity for use in biodiesel production. Since the crystal structures of most lipases have been solved, design of new lipases with new functions or improved properties are very much within reach using gene shuffling (directed evolution) or rational design protein. For example, the immobilized lipase producing Rhizopus oryzae whole cells developed by Matsumoto et al. (2001) mentioned in Section 6.8.3 have already been overexpressed in Saccharomyces cerevisiae. The engineered cells showed higher tolerance towards methanol in comparison to the natural cells. Isoform/isoenzyme of C. rugosa lipase named Lip2 has been engineered and produced, which may be useful in biodiesel production (Akoh et al., 2004). Yang et al. (2007) produced a methanol resistant and thermostable recombinant lipase in *B. cepacia* strain. The optimum temperature of the purified lipase was 70°C and was highly tolerant methanol, maintaining 98.3% of its activity in 50% methanol solution up to 48 h. The purified lipase was used to catalyze soybean oil transesterification and a biodiesel yield of 87.8% was reached after 72 h. Recently, Gao et al. (2009) cloned and expressed lipase gene from a lipase-producing Proteus sp. strain bacterium in a heterologous host, Escherichia coli. The recombinant E. coli expressing the lipase gene was applied in biodiesel production in the form of whole-cell biocatalyst. The whole-cell biocatalyst maintained its activity at methanol:oil molar ratio of 5:1 and 100% water by weight of the substrate. At the optimum temperature of 15°C, biodiesel yield of nearly 100% was reached after 12 h.

### 6.10.3 Supercritical fluids technology

As mentioned earlier, carrying on the reaction in organic solvent of high alcohol solubility has been suggested as an answer to problem of enzyme inhibition by short-chain alcohols. Although this results in an increased rate of reaction by operating at higher concentrations of alcohol, it is not recommended since it requires additional solvent recovery unit. Supercritical  $CO_2$  (SC- $CO_2$ ) offers the same advantages for lipase catalysis as organic solvents such as solubilization of the alcohol, simple recovery of the enzyme and favoring esterification to hydrolysis. In addition, SC- $CO_2$  offers more, such as product separation and easy recovery of the solvent. Moreover, it is non-flammable, non-toxic and inexpensive. The production of biodiesel in supercritical fluids (methanol) has been reported in the literature; however, just recently the coupled use of lipase with SC- $CO_2$  in the production of biodiesel has been reported (Rathore and Madras, 2007). Using supercritical fluids is usually expensive though, and more work is required in this regard to provide significant enhancement to the production of biodiesel and to offer biodiesel in competitive prices.

#### 6.10.4 Nano-technology

To minimize substrate diffusion limitations, enzymes are usually attached on nonporous materials. However, the non-porous supports exhibit low enzyme loading capabilities (Chen and Su, 2001). On the other hand, porous materials have high enzyme loading capabilities, but suffer from a high limitation of substrate (Hayashi *et al.*, 1993). In order to minimize the substrate diffusion limitation and enhance the enzyme loading at the same time, nano-size particles have been receiving great attention in recent years due to their large interfacial area and unique physical properties. Nanoparticle materials have been used in various bioprocesses including enzyme immobilization. For example, Tang *et al.* (2007) immobilized lipase onto nano-sized biopolymer Chitosan particles.

On the other hand, due to their high mechanical strength and thermal resistance, polyacrylonitrile (PAN) were used to generate electrospun nanofibrous membranes, which were used as the support for immobilizing *C. rugosa* lipase (Li and Wu, 2009). Lipase was bound covalently to PAN nanofibers ranged from 150 to 300 nm by amidination and used in a membrane reactor. The reactor was used for hydrolysis of oil and could also be used for biodiesel production.

Nano-sized magnetite (NSM) particles have been used as support for immobilization of enzymes. In addition to the larger surface area, due to the nanosize used, immobilization on magnetite materials allows easy enzyme recovery from the medium under the magnetic force, due to the magnetic response of the support material. Hence, there is no need for expensive liquid chromatography systems, centrifuges or filters. However, efficient loading of enzymes onto nano-sized magnetite (NSM) particles requires the surface functionalization by polymerization or sol-gel entrapment, which reduces the magnetic response of NSM particles (Lee et al., 2009). To avoid this limitation, Huang et al. (2003) immobilized lipase covalently to NSM particles. However, the covalent binding results in structural changes that can greatly reduce the activity of the enzyme. Therefore, coordinating NSM particles with a low molecular weight ligand has been proposed to overcome the abovementioned problem as the attachment would be via physical adsorption in this case, rather than by covalent bonding (Lee et al., 2009). At the same time, the particle sizes do not increase, as when the NSM particles are wrapped with polymers (Ma et al., 2003). In addition, the ligand acts as a spacer between NSM and the immobilized enzyme to prevent direct contact of lipase to the surface of the magnetites that may hinder the flexible enzyme structure. The immobilized lipase on the NSM particles showed higher specific activity and thermal stability than the free one and the activity of the immobilized lipase remained almost constant over five uses and recoveries (Bastida et al., 1998). The stable reuse as well as the convenience in the recovery offered by magnetic separation ensures that a surface-modified NSM particle is a good support material for lipase immobilization.

# 6.11 Sources of further information

Basic information on the kinetics of enzymatic reactions is available in the books of Bailey and Ollis (1986), Dutta (2008) and Shuler and Kargi (2001). These books present a biological background and provide a comprehensive introduction to biochemical engineering. Introduction to the genetic sequencing for producing proteins from recombinant DNA is also available in these books. However, an interested reader should refer to more specialized books (Martin and Christopher, 1990; Leskovac, 2003; Cook and Cleland, 2007) for more profound information, where much more is included about the structures of enzymes and the kinetics and mechanisms of enzymatic reactions. Enzymatic kinetics mechanism, relative rates of steps along the reaction pathway, and chemical mechanism, including acid-base chemistry and transition state structure for mono-, bis- and tri-substrate reactions are explained, and numerous general experimental protocols and kinetic data interpretation are described. In addition, a comprehensive catalog of enzymes in general, and lipase in particular, and their uses in modern manufacturing are available in the book of Polaina and Maccabe (2007) and the book of Uhlig (1998). These books survey general enzyme characteristics and discuss their microbiological origin, and stability of each enzyme. In addition, the most important industrial enzymes in use today are examined including immobilized enzymes.

As far as biodiesel is concerned, the book of Pahl (2005), 'Biodiesel: Growing a New Energy Economy', offers a comprehensive review from the history of the diesel engine to the development of the biodiesel industry, past, current and future. In addition, detailed information and news updates are available on the webpage of

the National Biodiesel Board (NBB) (http://www.biodiesel.org/). NBB is the national trade association representing the biodiesel industry in the United States.

### 6.12 References

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Production of glycerol-free and alternative biodiesels

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**Abstract:** In this chapter, the characteristics of novel type of biofuels integrating glycerol into their composition are described. The advantages of using biofuels integrating glycerol (Ecodiesel<sup>®</sup>, DMC-Biod<sup>®</sup>, Gliperol<sup>®</sup>) and the respective technologies to produce them are reported. In addition, the production of high-quality diesel fuel from vegetable oils by hydrotreating of triglycerides in conventional oil refineries is, also, reported.

Key words: Ecodiesel, DMC-Biod, Gliperol, hydrotreating of triglycerides.

### 7.1 Introduction

The soaring oil price has drastically increased the demand of fuels from renewable and biological sources. Consequently, the world research efforts are devoted to the study of new processes to efficiently produce these novel fuels. Current industrial production of *biodiesel* ('mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression diesel engines' - ASTM definition<sup>1</sup>) is carried out by homogeneous alkali-catalyzed transesterification of vegetable oils with methanol, using sodium hydroxide, potassium hydroxide or potassium methoxide as catalysts.<sup>2</sup> The homogeneous basic transesterification reaction shows a very fast kinetic rate, but unfortunately, there are, also, several environmental and economic problems associated with the process. A collateral saponification reaction takes place, reducing the biodiesel production efficiency. To prevent the biodiesel yield loss due to the saponification reaction, oil and alcohol must be dry and the oil should have a minimum amount of free fatty acids (FFAs) (less than 0.1% wt.). Biodiesel is finally recovered by repeated washing with water to remove glycerol, soap and excess of methanol.

In contrast, the acid transesterification allows to obtain a biodiesel production without formation of by-products. Drawbacks of an acid homogeneous transesterification include the use of corrosive catalysts ( $H_2SO_4$ ,  $H_3PO_4$ , HCl) and slow reaction rates. These may be increased at high temperatures and pressures, involving larger costs.<sup>3</sup> Methanol and oil are poorly soluble, so the reaction mixture contains two liquid phases. Other alcohols can be used, but they
are generally more expensive. Moreover, an acid pre-treatment is often needed in the homogeneous alkaline transesterification for oils having more than a 5 wt.% of FFAs in order to improve the biodiesel efficiency production.<sup>2–4</sup>

In any case (either in acid or basic catalysis), the process is far from being environmentally friendly, since the final mixture needs to be separated, neutralized and thoroughly washed, generating a great amount of waste in terms of salt residues. Moreover, the catalyst also cannot be recycled. These several additional steps inevitably put the total overall biodiesel production costs up, reducing at the same time the quality of the glycerol obtained as a by-product.<sup>5</sup> Several reports can be recently found on the production of biodiesel involving other chemical<sup>6,7</sup> or enzymatic catalytic protocols as greener alternatives.<sup>8,9</sup> The increasing environmental concerns have led to a growing interest in the use of enzyme catalysis, as these biocatalysts normally produce a cleaner biodiesel under milder conditions.<sup>10</sup> It also generates less waste than the conventional chemical process. Recent work demonstrates that heterogeneous enzymatic catalysts represent a potential solution to produce biodiesel from very low-quality triglycerides (TGs) feedstocks,<sup>11-14</sup> but in these cases, the cost of the enzymes has to be considered. The true limitation of the enzymatic method compared to the conventional base-catalyzed process deals with the alcoholysis of the 2-fatty acid esters of glycerol. Lipases have a peculiar 1,3-regioselectivity, which means that they selectively hydrolyze the more reactive 1 and 3 positions in the triglyceride.<sup>15</sup> In this regard, the production of biodiesel using lipases needs to take into account such regiospecific character.<sup>16,17</sup> In general, the challenging full alcoholysis of TGs involves long reaction times and gives conversions lower than 70 wt.% to fatty acid methyl or ethyl esters.<sup>18,19</sup>

A series of improvements in conversion levels and/or the use of methanol as alcohol to mimic the results of the base-catalyzed transesterification reaction are currently ongoing as a consequence of the present legal regulations for biodiesel (EN 14214). The current standard biodiesel production (under alkaline chemical conditions) is considered to be the most technically simple way to reduce the viscosity of vegetable oils from a range of 11–17 times<sup>20–22</sup> to just about twice of that of petroleum diesel. Various fuel properties of pure soybean oil, three B100 biodiesel types (soybean methyl esters, rapeseed methyl esters and rapeseed ethyl esters) and high-grade petro-diesel are summarized in Table 7.1.

The viscosity is the only significant parameter that may affect the performance of the diesel engine, as the other parameters are very similar. Interestingly, diglycerides (DGs) and TGs are mainly responsible for the increase in viscosity of pure vegetable oils. A novel biofuel containing fatty acid methyl esters/ monoglyceride (FAMEs/MG) or fatty acid ethyl esters/monoglyceride (FAEEs/ MG) blend (in which we exclude the presence of significant quantities of DGs and TGs) can be expected to have similar physical properties to those of conventional biodiesel, eliminating the production of glycerol as a by-product. The achievement of glycerol-free biofuels could be most convenient and advantageous in a market flooded by the production of glycerol as a by-product<sup>23–27</sup>

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Properties	Soybean oil	FAMEs <sup>a</sup>	FAMEs <sup>b</sup>	FAEEsc	D2
Specific gravity (g/cm <sup>3</sup> )	0.92	0.86	0.88	0.88	0.85
Viscosity (40°C)	46.7	6.2	5.65	6.11	2.98
Cloud point (°C)	2	-2.2	0	-2	-12
Pour point (°C)	0	-9.4	-15	-10	-18
Flash point (°C)	274	110	179	170	74
Boiling point (°C)	357	366	347	273	191
Cetane number	48.0	54.8	61.8	59.7	49.2
Sulphur (%wt.)	0.02	0.03	0.01	0.01	0.04
Heat of combustion (kJ/kg)	40.4	40.6	40.5	40.5	45.4

Table 7.1 Physico-chemical properties of soybean oil, biodiesel (B100) obtained from soybean oil and rapeseed oil and no. 2 diesel  $(D2)^{22}$ 

<sup>a</sup> FAMEs stands for fatty acid methyl esters from soybean oil.

<sup>b</sup> FAMEs stands for fatty acid methyl esters from rapeseed oil.

<sup>c</sup> FAEEs stands for fatty acid ethyl esters from rapeseed oil.

in the preparation of biodiesel. The aim of this chapter is to describe the characteristics and preparation of these novel types of biofuels integrating glycerol into their composition and the advantages of their use.

## 7.2 Novel types of biodiesel: biofuels that incorporate glycerol into their composition

Biodiesel production costs are mainly made up of three components: feedstocks costs, capital costs and by-product credits (glycerol). Particularly, the refined production cost of biodiesel is very close to the price of the feedstock because capital costs for biodiesel production are minimum and by-product glycerol has currently a very low value. However, if glycerol is integrated into biofuel composition, the production efficiency of this novel *biofuel* can be increased over 10%. The last step of washing and cleaning of the biodiesel in the conventional synthetic process [to clean the biodiesel and remove the traces of glycerol up to 0.02% glycerol (EN 14214)] can also be removed, reducing costs and generation of waste water.<sup>28</sup> High glycerol concentrations in the fuel cause various problems, including coking, viscosity increase and a potential dehydration to acrolein that can be further polymerized. Coking can also generate deposits of carbonaceous compounds on the injector nozzles, pistons and valves in standard engines, reducing the efficiency of the engines (Fig. 7.1).<sup>29,30</sup>

Recent investigations have also shown that minor components of biodiesel, usually considered contaminants under the biodiesel standard EN 14214, including FFAs and monoacyl glycerols or MGs, are essentially responsible for the lubricity of low-level blends of biodiesel and diesel fossil. Pure FAMEs exhibit a reduced lubricity compared to the biodiesel containing these



7.1 Dehydration (1), oxidation (2) and polymerization (3) reactions experienced by the residual glycerine in biodiesel into diesel engines.

compounds.<sup>31–36</sup> The presence of greater quantities of MGs and/or FFAs enhances the lubricity of biodiesel, which is another key feature of these novel biofuels that incorporates high amounts of MG, since their presence improves performance and preserves the life of the engines.

Three types of reported biofuels integrating glycerol (Ecodiesel<sup>®</sup>, DMC-Biod<sup>®</sup>, Gliperol<sup>®</sup>) and the respective technologies to produce them will be the subject of the following sections.

### 7.2.1 Ecodiesel®

Ecodiesel<sup>®</sup> is a biofuel incorporating glycerol, produced by enzymatic technology and patented by the University of Cordoba (UCO).<sup>37</sup> It is composed of two moles of FAEEs and a mole of MG. Particularly, Ecodiesel<sup>®</sup> is obtained using pig pancreatic lipase (PPL), in both free and immobilized form, to achieve the 1,3 selective transesterification of TGs to produce the corresponding 2-monoacyl derivatives of glycerol (MG) and two moles of FAEEs. Ethanol is the alcohol employed in the process (Fig. 7.2).



7.2 Transesterification of triglycerides with ethanol for Ecodiesel® production.

It is interesting to note that the enzymatic transesterification process can also be carried out with different short-chain alcohol (ethanol, 1- and 2-propanol, 1- and 2-butanol, etc.) and their mixtures, and it is not, in principle, restricted to the use of methanol, as it is normally under conventional chemical reactions (with acidic or basic catalysis).

Many reports on biodiesel preparation using free<sup>38</sup> or immobilized lipases can also be found.<sup>11–17</sup> In particular, PPL has been widely employed in the last decades for the resolution of mixtures of chiral enantiomers, either by enantioselective hydrolysis<sup>39,40</sup> or by alcoholysis or transesterification.<sup>41</sup>

The recent work of Luna *et al.* and their patents<sup>37,42</sup> show the entrapment of the PPL in demineralized sepiolite and its activity in the alcoholysis reaction of TGs contained in sunflower oil. Demineralized sepiolite is a clay mineral (a complex magnesium silicate) with a microporous structure and a channel dimension of  $11.5 \times 5.3$  Å. Its structure moves along fibres that confer a high specific surface area to the solid, similar to that of the AIPO-5.<sup>43,44</sup> The extraction of the ions (Mg<sup>2+</sup>, Al<sup>+3</sup>, etc.) by acid treatment significantly increases the size of the pores, making them comparable to those of amorphous silica<sup>45</sup> or even to a mesoporous structure similar to MCM-41.<sup>46</sup> These voluminous pores are able to trap some macromolecules including various enzymes.<sup>47,48</sup>

Results obtained by employing immobilized PPL compared to the free enzyme are reported in Table 7.2. Different temperatures, oil/alcohol ratios and oil/ immobilized PPL ratios have been also investigated and included in Table 7.3.

No. <sup>b</sup>	Temp. (°C)	Time (h)	FAEE (%)	MG + DG (%)	TG (%)	Yield (%)	Conv. (%)	TOF (mmol/h/g <sub>PPL</sub> )
Free PPL (0.01 g)	40	10	57.7	34.2	8.1	57.7	91.9	57.7
PPL filtrate (0.005 g)	40	10	26.9	38.2	34.9	26.9	65.1	53.8
1	25	72	61.3	38.7	_	61.3	100.0	8.4
2	30	24	58.7	41.3	_	58.7	100.0	21.7
3	39	24	55.2	32.6	12.2	55.2	74.5	23.1
4	40	24	58.8	41.2	_	58.8	100.0	24.5
5	45	20	61.1	38.9	_	61.1	100.0	25.6
6	50	27	60.8	39.2	—	60.8	100.0	30.5

Table 7.2 Comparison of activities of the free and immobilized PPL [composition, yield and conversion (% by GC) and TOF (mmol/h/g<sub>PPL</sub>)] in the ethanolysis of sunflower oil<sup>a</sup>

<sup>a</sup>Reaction conditions (unless otherwise stated): 12 ml sunflower oil (0.01 mol), 6 ml ethanol (0.11 mol), pH = 12, 0.5 g of demineralized sepiolite containing 0.01 g of immobilised PPL (0.1% w/w of total substrate).

<sup>b</sup>The 1 to 6 in the first column stands for the number of reuses of the immobilized PPL.

No.	Temp. (°C)	Time (h)	FAEE (%)	MG + DG (%)	TG (%)	Yield (%)	Conv. (%)	TOF (mmol/h/g <sub>PPL</sub> )
7	25	27	_	_	100.0			_
8	35	15	5.2	56.1	38.7	5.2	62.2	17.5
9	40	6	13.8	17.8	68.4	13.8	25.8	36.8
10	45	12	63.5	36.5	_	63.5	100.0	169.4
11	50	15	26.5	53.3	20.1	26.5	76.6	176.8

Table 7.3 Composition, yield and conversion (% by GC) and TOF (mmol/h/g\_{PPL}) of the Ecodiesel-100 obtained after the ethanolysis of sunflower oil<sup>a</sup>

<sup>a</sup>Reaction conditions: 48 ml sunflower oil (0.04 mol), 4.8 ml ethanol (0.09 mol), pH = 12, 0.5 g of demineralized sepiolite containing 0.01 g of immobilized PPL (0.1% w/w of total substrate).

Note: Data corresponds to the number of reuses (no.) of the biocatalyst, as a continuation of Table 7.2, under different reaction conditions.

The efficiency of the PPL can be obtained by comparing the turn-over frequency (TOF) values of free and immobilized PPL (Table 7.2), both obtained under the same experimental conditions and temperature. The efficiency of PPL was reduced to 42.5% [(24.5/57.7) × 100 = 42.5] after immobilization, due to a potential steric effect of the immobilized enzyme in the reaction and/or to the deactivation of the active sites of the enzyme in the entrapment process.

The TOF values showed that a decrease in the oil/alcohol molar ratio from 1:10 (Table 7.2) to 1:2 (Table 7.3) leads to an increase in the efficiency of the immobilized enzyme, in good agreement with the results obtained for the free enzyme. The results also pointed out that in any case, even with an excess of ethanol, a maximum 66% yield could be obtained, corresponding to a 1,3 selective enzymatic process. Of note was the enzyme stability and recyclability. Although the efficiency was reduced compared to the free form, the immobilization through physical entrapment of the PPL guaranteed the lifespan of the lipases. The free PPL was found to be completely deactivated in 48 hours, whereas the immobilized enzyme was active for several weeks, even after successive reuses preserving over 90% of the initial activity.

Another important advantage of the enzymatic process is the possibility of using various alcohols apart from methanol or ethanol. The effect of different short-chain alcohols on composition, yield, conversion and TOF of Ecodiesel-100, obtained in the alcoholysis of pure and waste frying sunflower oil, is reported in Table 7.4.

The biofuels could smoothly be obtained using the various alcohols employed, obtaining quantitative TGs conversions and selectivity to FAEE higher than 50% in most of the cases. The reaction typically takes 8–12 hours to complete, and the selectivity to FAEE increases with the time of reaction as expected.

Alcohol	Time (h)	FAE (%)	MG + DG (%)	TG (%)	Yield (%)	Conv. (%)	TOF (mmol/h.g <sub>PPL</sub> )
MeOH	24	55.1	44.9	_	55.1	100.0	22.9
EtOH	10	58.7	41.3	_	58.7	100.0	58.7
	24	60.7	39.3	_	60.7	100.0	25.5
EtOH 96%	10	27.8	72.2	_	27.8	100.0	27.8
	24	35.3	64.7	_	35.3	100.0	14.7
1-PrOH	16	56.9	43.1	_	56.9	100.0	35.6
	24	58.9	41.1	_	58.9	100.0	24.5
2-PrOH	16	19.6	80.4	_	19.6	100.0	12.3
	24	56.4	43.6	_	56.4	100.0	23.5
1-BuOH	16	47.5	42.2	10.3	47.5	89.7	29.7
	24	49.3	42.1	8.6	49.3	91.4	20.5
2-BuOH	13	59.6	40.4		59.6	100.0	45.8
	24	65.7	34.3	_	65.7	100.0	27.3
t-BuOH	24	52.3	38.3	9.4	52.3	100.0	21.8
1-PeOH	24	58.9	41.2	—	58.9	100.0	24.5

*Table 7.4* Effect of the different short-chain alcohols on composition, yield and conversion (% by GC) and TOF (turn over frequency) of the Ecodiesel-100, obtained in the alcoholysis of pure and waste frying sunflower oil

A potentially useful biofuel blend of FAEE, MG and traces of DG, in varying proportions (depending on the conversions), can be obtained. The FAEE/MG ratio was around 2:1 molar at quantitative triglyceride conversion.

In conclusion, the alcoholysis of TGs with short-chain alcohols using 1,3-regiospecific lipases can play an advantageous role, compared to the conventional base-catalyzed process, to obtain new biofuels incorporating glycerine and to minimize the waste production by improving the reaction conversion under greener conditions. Milder reaction conditions were employed and a cleaner biofuel (Ecodiesel-100) was obtained. The efficiency of PPL was remarkably increased at a higher pH in contrast with the reported results describing a poor activity of the enzymes at that pH. The immobilized PPL was highly stable, although the efficiency was reduced (42%) compared to the free enzyme. The catalyst can easily be recycled (11 times), almost preserving the initial catalytic activity.

## 7.2.2 DMC-Biod®

The transesterification reaction of TGs with dimethyl carbonate (DMC),<sup>49,50</sup> methyl acetate<sup>51,52</sup> or ethyl acetate<sup>53</sup> produces a mixture of FAMEs (or FAEEs) and cyclic glycerol carbonate esters of fatty acids (FAGCs) [or glycerol triacetate (triacetin)] (Fig. 7.3).



7.3 Transesterification of triglycerides with dimethyl carbonate for  $\mathsf{DMC}\text{-Biod}^{\textcircled{B}}$  production.

DMC-BioD<sup>®</sup> is a biofuel, patented by Notari *et al.*,<sup>54</sup> that integrates glycerol as glycerol carbonate in a process that can be developed by enzymatic technology,<sup>55</sup> but conventional basic catalyst (sodium methoxide – the same biodiesel obtained by vegetable oils and methanol, MeOH-biodiesel) can also be used.

The main problem of an enzymatic process is the inactivation of the enzyme (in this case of lipases) by some short-chain alcohol acyl acceptors such as methanol. In order to enhance the stability of lipases, the short-chain alcohols could be substituted by methyl acetate as acyl acceptors. But this solution needs a great amount of enzyme (three times more than in a normal alcoholysis) and an excessive amount of methyl acetate (1:12 of oil/methyl acetate) to obtain good conversion values. These drawbacks could be the main limitations for a potential industrial application of methyl acetate as acyl acceptor in the transesterification reaction of vegetable oils.

In this context, it is worthwhile exploring novel reagent as acyl acceptors to prepare esters from lipids. DMC is a potential candidate as a reagent for the transesterification of oils due to its eco-friendliness, chemical reactivity and physical properties.<sup>56</sup> DMC is neutral, odourless, cheap, non-corrosive, non-toxic and exhibits good solvent properties. Pioch *et al.* were the first researchers that reported ethyl oleate production by ethyl carbonate and oleic acid reaction catalyzed by an immobilized lipase.<sup>57</sup> The enzymatic transesterification of oil with DMC, as acyl acceptor, catalyzed by lipase, results in an irreversible reaction due to the decomposition of carbonic acid monoacyl ester into carbon dioxide and an alcohol, and consequently, the reaction is favoured towards its completion. Moreover, the DMC gives higher conversion than those of conventional acyl acceptors such as methanol or methyl acetate.

Different lipase sources and various vegetable oil feedstocks have been investigated. Some key parameters were explored to determine the optimal transesterification conditions, first of all the stability of the immobilized enzyme, in view of a potential scaling-up to industrial processes.<sup>55</sup> The main results concerning lipase sources and vegetable oils are summarized in Table 7.5.

From the screening results shown in Table 7.5, it is noticeable that Novozyme 435 (immobilized *Candida antarctica*) shows better activity towards all selected

Vegetable oil	Conversion (%)				
	<i>Mucor miehei</i> (Lipozyme IM)	Aspergillus niger	Porcine pancreas (Type II)	<i>Candida antarctica</i> (Novozyme 435)	<i>Candida</i> sp.
Soybean	1.3	_	6.8	59.4	22.8
Rapeseed	2.1	_	7.0	78.5	13.7
Corn	1.5	_	6.9	74.8	18.5
Sunflower	1.6	_	8.4	77.1	16.9
Cottonseed	2.2	_	7.2	67.7	15.1
Peanut	1.1	_	8.3	75.6	13.4
Olive	2.3	0.9	6.0	81.2	15.9
Castor	0.8	_	5.0	33.9	0.1
Sesame	1.3	_	6.8	39.7	17.3

Table 7.5 Transesterification of different vegetable oils with DMC in *n*-heptane using different immobilized lipases. $^{55}$ 

Note: Reaction conditions: 40°C, 150 rpm, oil/DMC molar ratio of 1:3, 10% enzyme based on oil weight, reaction time of 24 hours.

vegetable oils (81.2%, highest conversion with olive oil). Other lipases showed very little or no activity. Further results show that this lipase also exhibited high conversions in non-polar solvents (with the best performance using petroleum ether) and high activity with the optimum molar ratio of 1:4.5 for oil/DMC, using a DMC one-step addition. Concerning the optimum temperature reaction and the enzyme amount, Novozyme 435 strongly increases its activity with increasing quantities of the enzyme (optimum quantity was found to be 10% based on oil weight). Its performance gradually decreases above 50°C. Finally, concerning the more important parameter for an industrial application, the enzyme reusability, Su *et al.* showed that Novozyme 435 preserves up to 80% of its initial activity after five reaction cycles, if washed with acetone between each batch use.

The principal difference between DMC-BioD<sup>®</sup> and biodiesel produced from vegetable oil and methanol (MeOH-biodiesel) was the presence of FAGCs in addition to FAMEs. However, the mixture (FAMEs + FAGCs) has relevant physical properties to be employed as a fuel.<sup>54,58</sup> Flow and combustion properties of DMC-BioD<sup>®</sup>, relevant for its applications as a biofuel, are reported in Table 7.6.

Differences with respect to conventional biodiesel can be attributed to the presence of the FAGCs, which have a molecular weight larger than those of the corresponding FAMEs (see flash point and density). Nevertheless, the cetane number is almost the same but always lower than that of fossil diesel. DMC-BioD<sup>®</sup> has a higher viscosity than MeOH-biodiesel, but if blended with petroleum diesel, for example in a ratio of 20:80 v/v, the kinematic viscosity decreases to 3.3 cSt, a value closer to that of conventional diesel.

Properties	MeOH-biodiesel	DMC-BioD	Petroleum diesel
Cetane number	51	50	55
Density at 15°C (kg/m <sup>3</sup> )	0.885	0.887	0.830
Flash point (°C)	131	160	59
Lower heat value (MJ/kg)	35.6	36.3	41.4
Kinematic viscosity at 40°C (cSt)	4.1	5.6	3.5
Pour point (°C)	-3.8	-2	-8
Acid number (mg KOH/g)	< 0.5	0.3	_
Sulphate ashes (% mass)	< 0.02	0.002	0.05
Lubricity (WS 1.4µm)	209	213	_

Table 7.6 Properties of DMC-BioD and MeOH-biodiesel obtained from soybean oil<sup>58</sup>

Note: 20/80 v/v blend with petroleum diesel.

Moreover, the addition of DMC-BioD<sup>®</sup> at 20% level to diesel not only does not affect the fuel performance but also improves the lubricity of the diesel blend, which is a crucial factor for low-sulfur petroleum diesel. The lubricity value does not change significantly between MeOH-biodiesel and DMC-BioD<sup>®</sup>.

Last, but not least, from an economical point of view, the use of DMC in the transesterification reaction of vegetable oils will bring a minor impact on the overall biofuel costs: a large fraction of glycerol (> 65%) is incorporated into the biofuel in the form of FAGCs and a minor fraction is converted into glycerol carbonate and dicarbonate. These latter compounds could find utilization as additive and chemical intermediates, while, introducing into the market, glycerol carbonate and its derivatives (characterized by a low toxicity) can mitigate the problem of glycerol overproduction due to the increasing biodiesel utilization.<sup>58</sup>

## 7.2.3 Gliperol®

Gliperol<sup>®</sup> is another biofuel integrating glycerol recently patented by the Industrial Chemistry Research Institute of Warsaw (Poland).<sup>59</sup> It is composed of a mixture of three molecules of FAMEs and a molecule of glycerol triacetate (triacetin). It can be obtained after the transesterification of a mole of TG with three moles of methyl acetate using lipases or an ion-exchange acidic resin as catalysts.<sup>59–61</sup> When ethyl acetate is used, the corresponding FAEEs with triacetin are obtained,<sup>62</sup> following the enzymatic process summarized in Fig. 7.4.

In both processes, enzymatic and acidic, glycerol is not isolated as a by-product but utilized in the form of esters with low-molecular weight carboxylic acids as biofuel components. The methodology to prepare this novel biofuel employing heterogeneous catalyst allows the reduction of biofuel production costs by running the reaction without having to remove the catalyst. This allows to run the process in a continuous manner.<sup>59</sup> The process patented by the Industrial Chemistry Research Institute of Warsaw also consists of a post-treatment of the reaction

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7.4 Transesterification of vegetable oil with ethyl acetate for Gliperol<sup>®</sup> production.

mixture in order to remove, by distillation, excess of ester acidic alcohol used (ethyl acetate). Removal of the reactant from the mixture after reaction allows the reutilization of the reactant and, consequently, reduces the process costs.

In the case of an enzymatic process, immobilized lipases have been normally employed. Methyl or ethyl acetates can be used as acyl acceptors in the interesterification reaction, and the deactivation of enzyme by glycerol is minimized as no glycerol is produced in the reaction. Moreover, the use of ethyl acetate could be interesting because of the production of ethyl esters (an extra carbon atom) that increases the heat content and the cetane number of the final biofuel. Using ethyl esters instead of methyl esters also decreases the cold and pour points as well as increases the flash and combustion points, which improves cold starts and safety in handling the biofuel.<sup>63</sup> Modi et al. have obtained over 90% yield in ethyl esters by using 10% Novozyme 435 as lipase (wt/wt to sunflower oil) at 50°C after 12 hours, using an ethyl acetate/oil molar ratio of 11:1.<sup>62</sup> The reusability of the heterogeneous enzymatic catalyst (Novozyme 435) was also investigated in the same study, both in ethyl acetate and in ethanol. The stability of lipases after 12 reaction cycles was found to be constant: 91.3% and 93.7% as relative activity for interesterification and ethanolysis, respectively. Under these optimized conditions, Glyperol<sup>®</sup> production by enzymatic interesterification of vegetable oils could be technically and industrially feasible, nearly as much as the acidic process proposed by the Industrial Chemistry Research Institute of Warsaw.

A closing favourable point is also the good market of triacetin as a by-product. Triacetin has widespread applications in food, feed, printing, tanning, cigarettes, cosmetics, pesticides and pharmaceutical industries as well as in medical field.

# 7.3 Advantages in the use of biofuels integrating glycerol

Glycerol-free biofuels in a market flooded by the overproduction of glycerol from biodiesel utilization can be very convenient and advantageous. Ecodiesel<sup>®</sup>, DMC-Biod<sup>®</sup> and Gliperol<sup>®</sup> could be another good alternative for the future. They integrate glycerol as a by-product (MG, DMC or triacetin, respectively)

forming single homogeneous mixtures, thus avoiding the generation of waste or by-products in their preparation processes. Their preparation processes do not require any additional separation processes. MG, DMC or triacetin may be perfectly incorporated (and thus burned) with the mixture of FAMEs (or FAEEs) in diesel engines. In terms of green chemistry, glycerine incorporation into biofuels also increases the efficiency of the process (nominally from the current 90–100%), without causing substantial changes in the physical–chemical properties of biofuels. The atomic efficiency also experiences the corresponding improvement, given that the total number of atoms involved in the reaction is part of the final mixture that forms the biofuel.

The application of immobilized lipases, as heterogeneous enzymatic catalyst, may constitute a competitive procedure in the future, with respect to the current process based on basic homogeneous catalysis, because these biocatalysts are able to generate a novel family of biofuels that reduce the complexity of the process (avoid wash processes to remove the residual glycerine), increase the process yields and minimize waste generation. In addition, enzyme production processes are conducted in conditions that are comparatively more gentle (or green) to those conventionally utilized for the production of biodiesel (pH, temperature, pressure, etc.). With regard to combustion properties, relevant for the application of these biofuels in diesel engines, no important differences with respect to petroleum diesel have been found. Even better, properties including pour and cold points and lubricity are improved.

Finally, a very critical shortcoming, such as the use of water to clean/remove glycerol traces in biodiesel production, is also avoided by using these biofuels. This problem is a major issue in many southern European countries (e.g. Portugal, Italy, Spain, Greece) where draught can be a severe problem during summer.

In summary, biofuels integrating glycerol into their composition should be an urgent priority for the near future, as until now, none of them are legalized by the European Union despite several procedures being available to produce them.

## 7.4 Processing of oils and fats in the current oil refining plants

An alternative to transesterification of TGs contained in vegetable oils to obtain biofuels is to transform these renewable sources via different chemical processes in conventional petroleum refineries.

The production of high-quality diesel fuel from vegetable oils can be obtained by hydrocracking of TGs treated with high-molecular weight hydrocarbons in conventional oil refineries, as described by Huber *et al.*<sup>64</sup> In this way, renewable liquid alkanes can be produced by treatment of mixtures of vegetable oils and fractions of heavy oil vacuum (HVO), under hydrogen flows and conventional catalysts (sulphured NiMo/Al<sub>2</sub>O<sub>3</sub>) at standard temperature conditions (300– 450°C). The reaction involves the hydrogenolysis of C=C bonds in vegetable oils, which leads to a mixture of lower molecular weight alkanes by three different



7.5 Production of high-quality biodiesel from vegetable oils, through overall hydrotreatments, in conventional refineries.<sup>64</sup>

routes: decarbonylation, decarboxylation and hydrodeoxygenation (Fig. 7.5). Waxes can be formed. Straight-chain alkanes can be isomerized and cracked. The organic acids formed by hydrotreating could catalyze the isomerization and cracking reactions.

The yield of straight-chain alkanes  $C_{15}$ - $C_{18}$  obtained by hydrotreating of pure vegetable oil is about 71% (for sunflower oil), with a theoretical maximum yield of 75%. These yields can be increased by diluting pure vegetable oils with petroleum feedstocks such as HVO. The straight-chain  $C_{15}$ - $C_{18}$  yield of a 5% sunflower oil–95% HVO mixture has been reported to be 87%, higher than that obtained using pure sunflower oil (75%).<sup>64</sup>

In conclusion, the hydrotreating of vegetable oils also seems to be a promising alternative to produce biofuels from renewable sources, especially because it has the advantage of using existing petroleum refineries without the need to purchase additional capital equipment.

## 7.5 Future trends

TGs are the main components of different renewable sources. Biofuels feedstocks must not compete with food production. However, oil crops, waste cooking oil and animal fats themselves cannot satisfy the current world energy demand. For these reasons, first-generation biofuels, derived from sugarcane, cereal grains and oilseeds, have to be replaced with second- and third-generation biofuels. Second-generation biofuels come from special crops (non-edible seeds such as jatropha, brassica, etc.) or lignocellulosic materials. Algae and cyanobacteria for second/third-generation biodiesel production seem to be, currently, another potential renewable and carbon-neutral alternative to petroleum fuels.<sup>65</sup> Microalgae and cyanobacteria grow like plants; they need sunlight, carbon dioxide, water and inorganic salts to live, so producing microalgal biomass could be more expensive than growing crops. At the same time, most microalgae contain a great amount of

oil, from 20% to 80% of dry weight. Biodiesel production from oil extracted from microalgae can, also, use some of the carbon dioxide released by the power plants that burn fossil fuels, with evident environmental benefits.

However, large-scale microalgae can be currently produced only in raceway ponds or tubular photobioreactors.<sup>66,67</sup> Raceways use CO<sub>2</sub> much less efficiently than photobioreactors and algal productivity is very low because they are poorly mixed and a good light distribution is not there. In contrast, they are less expensive than photobioreactors. Tubular photobioreactors are made by arrays of transparent glass or plastic tubes, with about 0.1 m diameter, in which the sunlight is captured and the biomass grows. The efficiency of solar energy conversion is also limited by light penetration. Even if photobioreactors and ponds do not need arable/fertile soils, freshwater (many of the very efficient oil-producer organisms are marine: ponds near to the sea), pesticides and herbicides may also limit their widespread utilization. The acceptability of biodiesel quality obtained by microalgal biomass is another key issue. In fact, microalgal oils differ from most vegetable oils in being quite rich in polyunsatured fatty acids, with four or more double bonds (i.e. eicosapentaenoic acid C20:5n -3, five double bonds, or docosahexaenoic acid C22:6n-3, six double bonds). The unsaturation of an oil to biodiesel production is indicated by its iodine number (EN 14214 requires the iodine number of biodiesel to not exceed 120 g iodine/100 g biodiesel). Furthermore, the EN 14214 indicates limitations for polyunsatured methyl esters in the final biofuel: less than 1% (m/m). On the contrary, ASTM D6751 standardization does not indicate any limitation neither for iodine nor for polyunsatured FAMEs. Thus, from European Biodiesel Standards, many microalgal oils may need a pre-treatment (e.g. catalytic hydrogenation), in current refining oil plants, as described in the previous paragraph.

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# Biodiesel production from microbial oil

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**Abstract:** Biodiesel and bioethanol constitute the main biofuels produced currently at industrial scale from renewable resources (mainly oilseeds, waste oils, starchy crops and sucrose-rich biomass). However, the limited availability of conventional raw materials and/or the direct competition with food production restricts the growth of first-generation biodiesel and bioethanol production. In the last few years, there is a growing interest in biodiesel production from microbial oil accumulated by oleaginous microorganisms cultivated on waste streams from the food industry and agricultural residues. This chapter focuses on the description of the potential of microbial oil production by yeast and fungi, the biochemistry of oil accumulation and the prospect of biodiesel production from microbial oil.

**Key words:** biodiesel, microbial oil, biorefinery, oleaginous microorganisms, biomass.

## 8.1 Introduction

Bioethanol (mainly from sucrose and starchy crops) and biodiesel production (via transesterification of triglycerides) are the main first-generation biofuels that are currently produced on industrial scale. Biodiesel is produced by transesterification of triacylglycerols with short-chain alcohols (mainly methanol or ethanol) to produce monoalkyl esters, namely fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs). The worldwide production of biodiesel is mainly dependent on the utilization of waste oils, animal fats and oilseeds such as rapeseed, sunflower and soybeans. The recent food crisis has shown that research should focus on the development of second-generation biofuels generated from lignocellulosic raw materials and industrial waste streams (e.g. food industry wastes).

In the past few years, research has focused on the development of biodiesel production from single cell oil (SCO) that can be produced via fermentation using various oleaginous microorganisms (i.e. microorganisms that are able to accumulate lipids intra-cellularly at more than 20% of the total cellular dry weight). The proposed strategy may provide a more eco-efficient and sustainable option as compared to first-generation biofuels and second-generation bioethanol production routes utilising lignocellulosic biomass. Potential advantages include:

 The raw materials that will be used for the production of SCO-derived biodiesel do not compete with food production. In this way, cultivation of land for food production as well as industrial food processes could coincide with biodiesel production by utilizing residues and agro-industrial wastes.

- Microbial oil could be produced from various carbon sources (e.g. glucose, lactose, xylose, sucrose, glycerol) using natural microorganisms contrary to bioethanol production where natural microorganisms that are traditionally used in industrial processes utilize mainly glucose and sucrose.
- Bioethanol separation is an energy intensive technology with significant capital investment requirements, while separation of intra-cellularly accumulated SCO is likely to be achieved at significantly lower capital cost and energy requirements.
- Biodiesel production from oilseeds and waste oils will never provide adequate quantities of biodiesel to sustain the worldwide demand. In addition, the production cost of oilseeds is approximately 70–80% of the total biodiesel production cost. Biodiesel production from SCO will depend on the utilization of low-value waste streams or residues and therefore will offer a sustainable option for biofuel production.
- Transesterification of SCO results in the production of crude glycerine that could be used as a platform intermediate for the production of biofuels, chemicals and biodegradable plastics (Koutinas *et al.*, 2007a; Aggelis, 2009).

## 8.2 Microorganisms and raw materials used for microbial oil production

There are many microalgae, yeasts (e.g. Candida, Cryptococcus, Lipomyces, Rhodotorula, Rhodosporidium, Trichosporon), fungi (e.g. Mortierella, *Cunninghamella*) and bacteria that can accumulate intra-cellularly high amounts of SCO that has fatty acid composition similar to vegetable oils (Meng et al., 2009). Microorganisms can be characterized as oleaginous in the case that they can accumulate SCO to more than 20% of their total cellular dry weight (Ratledge, 1991). SCO could be used either for value-added applications (e.g. food additives) or commodity uses (e.g. biodiesel production). The industrial application of SCO for biodiesel production is dependent on the development of a fermentation process that provides high carbon source to SCO conversion vields, high productivities, high lipid content in cellular biomass and high SCO concentrations. The previous criteria constitute a useful tool so as to select the appropriate microorganisms that will facilitate the industrial implementation of biodiesel production from SCO. For instance, microalgae may accumulate high amounts of microbial lipids but they cannot compete with oleaginous yeast and fungi because their cultivation requires a big area and long fermentation duration. Furthermore, bacteria may achieve high growth rates but the majority of bacterial strains accumulate relatively low amounts of SCO (up to 40% of total cellular dry weight) (Meng et al., 2009). Some yeast strains (e.g. Rhodosporidium sp., Rhodotorula sp., Lipomyces sp.) may accumulate intra-cellularly around 70%

(w/w) of SCO (Guerzoni *et al.*, 1985; Li *et al.*, 2007; Angerbauer *et al.*, 2008; Meng *et al.*, 2009).

Table 8.1 shows that mainly yeasts and some fungi may offer appropriate cell factories for the production of SCO. Table 8.1 clearly demonstrates that cell densities up to 185 g/L with a lipid content up to 67.5% (w/w) have been achieved mainly in fed-batch cultures or continuous fermentations with recycling (Yamauchi *et al.*, 1983; Pan *et al.*, 1986; Ykema *et al.*, 1988; Meesters *et al.*, 1996; Li *et al.*, 2007). In many cases, SCO has similar fatty acid composition as in the case of vegetable oils used for biodiesel production. SCO is mainly composed of triacylglycerols – TAGs – with a fatty acid composition rich in C<sub>16</sub> and C<sub>18</sub>, namely palmitic (16:0), palmitoleic (16:1), stearic (18:0), oleic (18:1) and linoleic (18:2) acids (Meesters *et al.*, 1996; Ratledge and Wynn, 2002; Li *et al.*, 2007; Meng *et al.*, 2009). The SCO produced by *C. curvatus* has similar composition to palm oil (Davies, 1988). The SCO produced by *Yarrowia lipolytica* contains stearic, oleic, linoleic and palmitic acid (Papanikolaou *et al.*, 2002a).

There is a remarkable plethora of (pure or raw agro-industrial) substrates that can be used by oleaginous microorganisms for microbial growth and accumulation of microbial lipids (Table 8.1). Production of SCO implicates utilization of pure sugars as substrates (e.g. analytical glucose, lactose, etc.) (Moreton, 1985; Moreton and Clode, 1985; Aggelis et al., 1996; Papanikolaou et al., 2004a, 2004b; Li et al., 2007; Zhao et al., 2008; Fakas et al., 2009a), sugar-based renewable materials or sugar-enriched wastes (Ykema et al., 1989, 1990; Davies et al., 1990; Papanikolaou et al., 2007a; Fakas et al., 2006, 2007, 2008a, 2008b, 2009a), vegetable oils (Bati et al., 1984; Koritala et al., 1987; Aggelis and Sourdis, 1997), crude-waste industrial hydrophobic materials (e.g. industrial free-fatty acids, waste fats, crude fish oils, soap-stocks etc) (Guo et al., 1999; Guo and Ota, 2000; Papanikolaou et al., 2001, 2002a, 2007b; Papanikolaou and Aggelis, 2003a, 2003b), pure fatty acids (Mličková et al. 2004a, 2004b) or glycerol (Meesters et al., 1996; Papanikolaou and Aggelis 2002; Mantzouridou et al., 2008; André et al., 2009; Makri et al., 2010). This indicates that it is feasible to utilize various natural resources for the production of SCO providing the opportunity to develop processes producing SCO-derived biodiesel either integrated in existing food industries or as individual production plants (e.g. in agricultural areas so as to utilize various lignocellulosic feedstocks).

Starch-based waste or by-product streams (e.g. wheat flour milling by-products, waste bread, flour-based waste or by-product streams from the confectionary industry) generated by the food industry or collected as disposed food by dedicated companies could be used for the production of glucose-based fermentation media. Wheat flour milling by-products has been considered for the production of biofuels and platform chemicals (Neves *et al.*, 2007; Dorado *et al.*, 2009) and therefore could be regarded as a potential feedstock for the production of SCO-derived biodiesel. In the case of SCO production, certain oleaginous microorganisms have the ability to consume both glucose and xylose. This

Table 8.1 SCO product	ion from various mic	roorganisms, carbon	sources and cu	ltivation modes		
Microorganism	Cultivation mode	Carbon source	Total dry weight (g/L)	MO content (%, w/w)	Productivity (g L <sup>-1</sup> h <sup>-1</sup> )	Reference
Yeast species Yarrowia lipolytica	single-stage	Glucose	9.2	25	0.08	Aggelis and
Yarrowia	continuous single-stage	Crude glycerol	8.1	43	0.11	Komaitis, 1999 Papanikolaou and
lipolytica Varrowia	continuous chaka flack	Stearin	15.2	50	Ø N	Aggelis, 2002 Pananikolaou
lipolytica			1.0	10		et al., 2007b
Candida sp. 107	single-stage continuous	Glucose	18.1	37.1	0.4	Gill <i>et al.</i> , 1977
	single-stage continuous	Glucose	13.5	29	0.16	
	single-stage continuous	Sucrose	16	28	0.18	
Candida curvata	single-stage continuous	Lactose	18	31	0.22	Evans and Ratledae, 1983
	single-stage continuous	Xylose	15	37	0.27	
	single-stage continuous	Ethanol	11.5	35	0.2	
Apiotrichum curvatum	batch	Glucose	14.5 21 6	45.6 26	N.A.	Hassan <i>et al.</i> , 1993 Viomo et al., 1993
	recvoling	VVIIGY	2.1.0 85	35	0.372	
	continuous		20	36	0.382	
	partial recycling		91.4	33	0.995	
Cryptococcus curvatus	fed-batch	Glycerol	118	25	0.59	Meesters <i>et al.</i> , 1996
Lipomyces starkeyi	shake flask	Glucose & Xylose	20.5	61.5	N.A.	Zhao <i>et al.</i> , 2008
Lipomyces starkeyi	shake flask	Glucose & sewaae sludae	9.4	68	N.A.	Angerbauer <i>et al</i> 2008

Lipomyces starkeyi	fed-batch	Glucose	153	54	0.59	Yamauchi <i>et al.</i> , 1983
		Glucose	24.1	56.6	N.A.	
		Sucrose	19.5	62.6	N.A.	
		Xylose	17.1	57.8	N.A.	Zhu <i>et al.,</i> 2008
Trichosporon	shake flask	Lactose	16.9	49.6	N.A.	
fermentans		Fructose	21.5	40.7	N.A.	
		Molasses	36.4	35.3	N.A.	
Trichosporon	shake flask	Rice straw	28.6	40.1	N.A.	Huang <i>et al.</i> , 2009
fermentans		hydrolysate				
		Mannose	22.7	50.4	N.A.	
		Galactose	23.6	59	N.A.	
		Cellobiose	15.8	65.6	N.A.	
Rhodosporidium toruloides	fed-batch	Glucose	106.5	67.5	0.54	Li <i>et al.</i> , 2007
Bhodotorula gracilis	continuous	Glucose	9 60	49.8	0 096	Choi <i>et al</i> 1982
			00.0 L			
Rhodotorula	snake tlask	Monosodium	GZ	20	N.A.	Xue <i>et al.</i> , 2008
glutinis		glutamate				
		wastewater				
Rhodotorula glutinis	fed-batch	Glucose	185	40	0.88	Pan <i>et al.</i> , 1986
Fungal species						
Cunninghamella	shake flask	Glucose	15	46	N.A.	Fakas <i>et al.</i> , 2009a
echinulata						
Cunninghamella	shake flask	Starch	13.5	28	N.A.	Papanikolaou
echinulata						<i>et al.</i> , 2007a
		Pectin	4.1	10	N.A.	
Mortierella isabellina	shake flask	Glucose	27	44.6	N.A.	Fakas <i>et al.</i> , 2009a
Mortierella	shake flask	Starch	10.4	36	N.A.	Papanikolaou
isabellina						<i>et al.</i> , 2007a
		Pectin	8.4	24	N.A.	
Mucor sp. RRL001	shake flask	Tapioca starch	28	17.8	N.A.	Ahmed <i>et al.</i> , 2006
Mortierella	commercial-scale	Glucose	62	46.1	N.A.	Hiruta <i>et al.</i> , 1997
ramanniana	batch bioreactor					

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indicates that it will be feasible to consume the major carbon sources in wheat flour milling by-products (i.e. glucose from starch and xylose from hemicelluloses). Waste bread and other starch-based food could be collected prior to disposal by dedicated companies and could be used for the production of SCO derived biodiesel. Waste bread has been evaluated for the production of bioethanol (Ebrahimi *et al.*, 2008). Furthermore, waste or by-product streams from the confectionary industry that contain mainly starch and sucrose as carbon sources could be considered as potential feedstocks for SCO production.

Other waste streams from the food industry that could be used for the production of SCO-derived biodiesel are whey and molasses. Whey constitutes a significant waste stream from the dairy industry and its valorization is an important environmental target. The yeast strain *Cryptococcus curvatus* can accumulate intra-cellularly a SCO content of around 60% (w/w) of the total cell dry weight during fermentation on whey or other agricultural and food processing wastes (Ratledge 1991; Meesters *et al.*, 1996). In addition, molasses (a by-product from sugar refining) has been used as fermentation medium in shake flask cultures for the production of SCO by the yeast *Trichosporon fermentans* to produce 36.4 g/L total dry weight with an SCO content of 35.3% (w/w) (Zhu *et al.*, 2008).

As indicated in Table 8.1, certain oleaginous microorganisms can utilize glycerol for the production of SCO (Meesters *et al.*, 1996; Papanikolaou and Aggelis, 2002). Therefore, crude glycerol generated from biodiesel production plants could be recycled for the production of SCO-derived biodiesel. More importantly, the ability of some oleaginous microorganisms to consume various sugars derived from lignocellulosic biomass (e.g. xylose, mannose, galactose, cellobiose) could lead to the utilisation of lignocellulosic biomass for the production of SCO-derived biodiesel (Zhu *et al.*, 2008; Huang *et al.*, 2009).

Biorefineries should depend entirely on crude biological entities for the formulation of fermentation media that will contain all the necessary nutrients for microbial growth and SCO accumulation. In order to implement this principle, protein-rich industrial waste streams should be used for the production of fermentation media enriched in organic sources of nitrogen (e.g. amino acids, peptides), phosphorus, minerals, vitamins and trace elements. Such nutrient supplements for fermentation processes could be produced from oilseed residues generated after oil extraction in the first-generation biodiesel production plants (e.g. protein-rich rapeseed or sunflower cakes), meat-and-bone meal, sewage sludge, protamylase (residual stream enriched in amino acids and peptides that is generated during the industrial production of starch from potatoes), corn steep liquor and residual yeast from potable or fuel ethanol production plants. Protein and other nutrients are also contained together with carbon sources in various food waste streams (e.g. waste bread, whey). Therefore, in many cases, a single waste stream from the food industry could be sufficient for the production of nutrient-complete fermentation media for SCO production. It should be stressed that organic N-sources may enhance lipid accumulation (even two or three times higher than the amount of lipids accumulated with inorganic N-sources) in certain oleaginous microorganisms (e.g. *Rhodosporidium toruloides*, *Trichosporon cutaneum* and *T. fermentans*) (Evans and Ratledge, 1984a, 1984b; Zhu *et al.*, 2008).

The conversion of waste streams into fermentation media would require the development of advanced upstream processing strategies that exploit the full potential of complex biological entities. Similar upstream processing schemes have been developed in the case of cereal conversion into bioethanol, biodegradable plastics and platform chemicals (Arifeen *et al.*, 2007; Koutinas *et al.*, 2007b; Du *et al.*, 2008; Xu *et al.*, 2010). In addition, pre-treatment technologies that have been developed for the generation of fermentation feedstocks for bioethanol production could be adapted in the case of SCO-derived biodiesel production (Lloyd and Wyman, 2005; Zhu *et al.*, 2009).

Based on the maximum theoretical conversion yields of glucose to SCO (0.33 g/g) and bioethanol (0.51 g/g) and the lower heating values (LHVs) for SCOderived biodiesel (37.5 MJ/kg) and bioethanol (26.7 MJ/kg), then the LHV per kg glucose that could be generated via fermentative production of SCO and bioethanol is 9% higher in the case of ethanol. However, the overall energy balance (output/ input) could be favourable in the case of SCO-derived biodiesel because it is expected that the energy required to produce biodiesel after SCO fermentation would be lower than the energy required to purify bioethanol from fermentation broths. This will also result in surplus lignin that will be used for chemical production when lignocellulosic biomass is used as raw material. In the case of bioethanol production, all lignin is required for energy generation for the plant. In addition, biodiesel production from SCO would create a sustainable supply of glycerol that is regarded as an important building block for the chemical industry. For instance, we could combine biodiesel production from SCO with biodegradable polymer (e.g. polyhydroxyalkanoates) and platform chemical (e.g. 1,3-propanediol, succinic acid, itaconic acid) production from crude glycerol generated during biodiesel production (Jarry and Seraudie, 1997; Papanikolaou et al., 2000; Lee et al., 2001). We should also highlight the well-understood efficiency of diesel engines which lead to a lower level of CO<sub>2</sub> emitted per kilometre travelled.

# 8.3 The biochemistry of lipid accumulation in the oleaginous microorganisms

### 8.3.1 General remarks

When various sugars or similarly metabolized compounds (e.g. glycerol, polysaccharides, etc.) are utilized for the production of SCO, accumulation of lipid in the microbial cells or mycelia (the so-called '*de novo*' lipid accumulation process) is triggered by exhaustion of nitrogen from the growth medium, which allows the conversion of sugar to storage lipid (Ratledge, 1988, 1994; Ratledge and Wynn, 2002; Wynn and Ratledge, 2006; Papanikolaou and Aggelis, 2009;

Fakas *et al.*, 2009b). In contrast, when growth is conducted on hydrophobic carbon sources (e.g. fats, oils), accumulation of storage lipids (the so-called '*ex novo*' lipid accumulation process) is a primary anabolic process occurring simultaneously with the production of lipid-free material, being independent from the nitrogen exhaustion in the medium (Fickers *et al.*, 2005; Papanikolaou and Aggelis, 2010).

In the case of SCO utilization for biodiesel production, research interest is focused only upon the process of *de novo* lipid accumulation. In this case, there is continuously increasing interest upon the potentiality of transforming abundant renewable materials (like waste glycerol, flour-rich waste streams, cellulose and hemicellulose hydrolysates, etc.) into SCO that will be further transformed into biodiesel. The process of *ex novo* lipid accumulation aims at adding value to low-cost fatty materials so that speciality high-value lipids (e.g. cocoa-butter or other exotic fats substitutes) will be produced (Papanikolaou *et al.*, 2001; 2003; Papanikolaou and Aggelis 2003a, 2003b, 2010).

The lipids produced by oleaginous microorganisms are mainly composed of neutral fractions [principally triacylglycerols (TAGs) and to lesser extent sterylesters (SEs)] (Ratledge, 1994; Ratledge and Wynn, 2002). As a general remark it must be stressed that when growth is carried out on various hydrophobic substances, the microbial lipid produced contains lower quantities of accumulated TAGs compared with growth elaborated on sugar-based substrates (Koritala *et al.*, 1987; Guo *et al.*, 1999; Kinoshita and Ota, 2001; Papanikolaou *et al.*, 2001, 2002a; Fakas *et al.* 2006, 2007, 2008a). In any case, accumulation of storage lipids is accompanied by morphological changes in the oleaginous microorganisms, since 'obese' cells with large lipid globules can generally appear during the lipid-accumulating phase (Figure 8.1). Storage lipids, unable to integrate into



8.1 'Obese' cells of the yeast *Yarrowia lipolytica* with large lipid globules appeared during lipid-accumulating growth phase. Magnification  $\times 100$  (Makri *et al.*, 2010).



8.2 Lipid bodies in the yeast *Yarrowia lipolytica* as shown by electron microscopy (Mličková *et al.*, 2004a).

phospholipid bi-layers, cluster to form the hydrophobic core of the so-called 'lipid bodies' or 'oil bodies' (Mličková *et al.*, 2004a, 2004b). Lipid bodies of the oleaginous *Y. lipolytica* yeast are illustrated in Figure 8.2. As previously stressed, the biochemical pathways of *de novo* and *ex novo* lipid accumulation process present fundamental differences. These differences will be presented, explained, clarified and comprehensively discussed in the following sections.

# 8.3.2 Lipid accumulation from fermentation of sugars and related substrates used as the sole carbon source

De novo accumulation of cellular lipids is an anabolic biochemical process in which, by virtue of quasi-inverted  $\beta$ -oxidation reaction series, acetyl-CoA issued by the intermediate cellular metabolism, generates the synthesis of intra-cellular fatty acids. Fatty acids will be then esterified in order to synthesize structural (phospholipids, sphingolipids, etc.) and reserve lipids (TAGs and SEs) (Moreton, 1988; Ratledge, 1988, 1994; Davies and Holdsworth, 1992; Ratledge and Wynn, 2002; Papanikolaou and Aggelis, 2009). In oleaginous microorganisms in which de novo lipid accumulation is conducted, acetyl-CoA that constitutes the precursor of intra-cellular fatty acids, derives from breakdown of citric acid that under some circumstances cannot be catabolized through the reactions performed in the Krebs cycle, but it is accumulated inside the mitochondria. This occurs when its concentration becomes higher than a critical value resulting in citric acid transportation into the cytosol (Ratledge, 1988, 1994; Ratledge and Wynn, 2002; Wynn and Ratledge, 2006; Fakas et al., 2009b). The key-step for citric acid accumulation inside the mitochondrion matrix is the change of intra-cellular concentration of various metabolites, conducted after exhaustion of some nutrients (mainly nitrogen) in the culture medium (Ratledge, 1988, 1994; Ratledge and Wynn, 2002; Wynn and Ratledge, 2006). This exhaustion provokes a rapid decrease of the concentration of intra-cellular AMP, since, by virtue of AMPdesaminase, the microorganism cleaves AMP into IMP and  $NH_4^+$  ions in order to utilize nitrogen, in the form of  $NH_4^+$  ions, as a complementary nitrogen source, necessary for synthesis of cell material (Evans and Ratledge, 1985).

The excessive decrease of intra-cellular AMP concentration alters the Krebs cycle function; the activity of both NAD<sup>+</sup> and NADP<sup>+</sup>-isocitrate dehydrogenases, enzymes responsible for the transformation of iso-citric to  $\alpha$ -ketoglutaric acid, lose their activity, since they are allosterically activated by intra-cellular AMP, and this event results in the accumulation of citric acid inside the mitochondrion (studies performed in the oleaginous microorganisms Candida sp. 107, Rhodosporidium toruloides, Y. lipolytica, Mortierella isabellina, Mortierella alpina, Mucor circinelloides and Cunningamella echinulata) (Botham and Ratledge, 1979; Evans and Ratledge, 1985; Wynn et al., 2001; Finogenova et al., 2002; Papanikolaou et al., 2004b). When the concentration of citric acid becomes higher than a critical value, it is secreted into the cytosol. Finally, in the case of lipogenous (lipidaccumulating) microorganisms, cytosolic citric acid is cleaved by ATP-citrate lyase (ACL), the key-enzyme of lipid accumulation process in the oil-bearing microorganisms, in acetyl-CoA and oxaloacetate, with acetyl-CoA being converted, by an inversion of  $\beta$ -oxydation process, to cellular fatty acids. In contrast, nonoleaginous microorganisms (e.g. various Y. lipolytica and Aspergillus niger strains) secrete the accumulated citric acid into the culture medium (Ratledge, 1994; Anastassiadis et al., 2002; Papanikolaou et al., 2002b) instead of accumulating significant quantities of reserve lipid. In general, production of citric acid by citrate-producing strains is a process carried out when extra- and hence intracellular nitrogen is depleted [overflow metabolism phenomenon (see Anastassiadis et al., 2002), while studies of the intra-cellular enzyme activities and co-enzyme concentrations have somehow identified and clarified the biochemical events leading to citric acid biosynthesis (Finogenova et al., 2002; Morgunov et al., 2004; Makri et al., 2010) and indeed it has been demonstrated that citric acid secretion and SCO accumulation are processes indeed identical into their first steps.

In a third category of microorganisms, the accumulated (inside the cytosol) citric acid provokes inhibition of the enzyme 6-phospho-fructokinase, and the above fact results in the intra-cellular accumulation of polysaccharides based on the 6-phospho-glucose (Evans and Ratledge, 1985). Schematically, the intermediate cellular metabolism resulting in the synthesis of either citric acid or storage lipid is presented in Figure 8.3 (Ratledge, 1994; Ratledge and Wynn, 2002; Papanikolaou and Aggelis, 2009).

After the biosynthesis of intra-cellular fatty-CoA esters, an esterification with glycerol takes place in order for the reserve lipids to be stocked in the form of TAGs (Ratledge, 1988, 1994). This synthesis in the oleaginous microorganisms is conducted by virtue of the so-called pathway of  $\alpha$ -glycerol phosphate acylation (Ratledge, 1988; Davies and Holdsworth, 1992; Athenstaedt and Daum, 1999; Müllner and Daum, 2004; Fakas *et al.*, 2009b). In this metabolic pathway, free fatty acids are activated by coenzyme A and are subsequently used for the acylation of the glycerol backbone to synthesize TAGs. In the first step of TAGs assembly, glycerol-3-phosphate (G-3-P) is acylated by G-3-P acyltranferase (GAT) at the sn-1 position to yield 1-acyl-G-3-P (lysophospatidic acid-LPA), which is then



*8.3* Pathways involved in the breakdown of glucose by microbial strains capable of producing SCO and/or citric acid in nitrogen-limited conditions. FFA: free-fatty acids; TRSP: citric acid transporting system; a, b, c: systems transporting pyruvic acid from cytosol to mitochondrion and inversely; d: system transporting citric and malic acid from cytosol to mitochondrion and inversely; ACL: ATP-citrate lyase; FAS: fatty acid synthetase; ICDH: iso-citrate dehydrogenase; MD<sub>c</sub>: malate dehydrogenase (cytoplasmic); MD<sub>m</sub>: malate dehydrogenase; CS: citrate synthase; ICL: iso-citrate lyase; EMP: Embden-Mayerhoff-Parnas pathway. Pathways described by Ratledge (1994), Ratledge and Wynn (2002), Papanikolaou and Aggelis (2009).

further acylated by lysophosphatidic acid acyltransferase (also named 1-acyl-G-3-P acyltransferase-AGAT) in the sn-2 position to yield phosphatidic acid (PA). This is followed by dephosphorylation of PA by phosphatidic acid phosphohydrolase (PAP) to release diacylglycerol (DAG). In the final step DAG is acylated either by diacylglycerol acyltransferase or phospholipid diacylglycerol acyltransferase to produce TAGs (Ratledge, 1988; Davies and Holdsworth, 1992; Athenstaedt and Daum, 1999; Müllner and Daum, 2004; Fakas *et al.*, 2009b).

As far as the structure of the microbial TAGs produced is concerned, although their final composition could theoretically be a random substitution of acyl-CoA groups into glycerol, in the case of the oleaginous microorganisms that have been examined, the glycerol sn-2 position is almost always occupied by unsaturated fatty acids [production of vegetable-type TAGs (see Ratledge, 1988; 1994; Guo and Ota, 2000)]. Therefore, various oleaginous microorganisms (principally yeasts belonging to the species *Rhodosporidium toruloides*, *Apiotrichum curvatum* and *Y. lipolytica*) have long been considered as promising candidates for the production of equivalents of exotic fats (fats that are principally saturated but containing unsaturated fatty acids esterified in the sn-2 glycerol position) (Moreton 1985, 1988; Moreton and Clode 1985; Ykema *et al.*, 1989, 1990; Davies *et al.*, 1990; Lipp and Anklam, 1998; Papanikolaou *et al.*, 2001, 2003; Papanikolaou and Aggelis 2003b; Papanikolaou and Aggelis, 2010).

# 8.3.3 Lipid production from fermentation of hydrophobic materials used as the sole carbon source

It is known that when microorganisms are cultivated on fat-type substrates (e.g. long-chain free-fatty acids, TAGs, fatty-esters, etc.) production of (intracellular, cell-bounded or extra-cellular) lipases is performed as a physiological response to the presence of fatty materials into the growth medium (Fickers et al., 2005). This secretion is obligatory in the case that TAGs or fatty-esters are used as substrates (Fickers et al., 2005; Papanikolaou and Aggelis, 2010). In contrast, a large variety of microorganisms are capable of utilizing soaps as well as freefatty acids as sole carbon and energy source, regardless of the lipolytic capacities of the microorganisms used in order to break down fatty materials (Ratledge and Boulton, 1985; Papanikolaou and Aggelis, 2010). Specifically, for the case of the yeast Y. lipolytica, its culture on TAG-type substrates is accompanied by secretion of an extra-cellular lipase called Lip2p, encoded by the LIP2 gene (Pignède et al., 2000). This gene encoded for the biosynthesis of a precursor premature protein with Lys-Arg cleavage site. The secreted lipase was reported to be a 301-aminoacid glycosylated polypeptide which belongs to the TAGs hydrolase family (EC 3.1.1.3) (Pignède et al., 2000; Fickers et al., 2005). The Lip2p precursor protein was processed by the KEX2-like endoprotease encoded by the gene XPR6, whereas deletion of the above gene resulted in the secretion of an active but fewer stable pro-enzyme (Pignède et al., 2000). Simultaneously, other intra-cellular lipases (Lip7p, Lip8p) may also be produced and secreted into the culture medium, that present different fatty acid specificities, with maximum activity being displayed against  $^{\Delta 9}18:1$  (oleic acid), 6:0 (capronic) and 10:0 (caprinic) fatty acids (Fickers et al., 2005).

The free-fatty acids (existed as initial substrate or produced after lipase hydrolysis of the TAGs/fatty-esters) will be incorporated, with the aid of active transport, inside the microbial cell. It is interesting to state that for the case of *Y. lipolytica* yeast, the various individual substrate fatty acids would be removed from the medium (and hence incorporated inside the microbial cell) with different

rates (Papanikolaou *et al.* 2001, 2002a; Papanikolaou and Aggelis, 2003b). Specifically, regardless of the initial concentrations of the extra-cellular fatty acids, the incorporation rate of the lower aliphatic chain (lauric acid-12:0 and myristic acid-14:0) or unsaturated ( $^{A9}18:1$  and linoleic acid- $^{A9,12}18:2$ ) fatty acids is significantly higher than that of principally stearic (18:0) and to lesser extent palmitic (16:0) acid (Papanikolaou *et al.*, 2001; Papanikolaou and Aggelis, 2003b). Moreover, the incorporated fatty acids will be either dissimilated for growth needs or become a substrate for endo-cellular bio-transformations (synthesis of 'new' fatty acid profiles which did not exist previously in the substrate) (Ratledge and Boulton, 1985; Koritala *et al.*, 1987; Aggelis and Sourdis, 1997; Guo *et al.*, 1999; Kinoshita and Ota, 2001; Papanikolaou *et al.*, 2001, 2002a, 2007b; Papanikolaou and Aggelis, 2003a, 2003b, 2010).

The intra-cellular dissimilation of the various catabolized fatty acids is performed by reactions catalyzed by the various intra-cellular acyl-CoA oxidases (Aox). A significant amount of experimental work has been performed in relation with the elucidation of the above-mentioned reactions by using strains of the nonconventional yeast Y. lipolytica (Fickers et al., 2005). In fact, it has been revealed that the aforementioned biochemical process is a multi-step reaction requiring different enzymatic activities of five acyl-CoA oxidase isozymes (Aox1p through Aox5p), encoded by the POX1 through POX5 genes (Luo et al. 2002; Mličková et al. 2004a, 2004b; Fickers et al. 2005). Aox3p is specific for short chain acyl-CoAs, Aox2p preferentially oxidizes long-chain acyl-CoAs while Aox1p, Aox4p and Aox5p do not appear to be sensitive in the chain length of the aliphatic acyl-CoA chain (Mauersberger et al. 2001; Luo et al. 2002; Fickers et al. 2005). It should also be noticed that genetically modified strains of Y. lipolytica namely JMY 798 (MTLY 36-2P) and JMY 794 (MTLY 40-2P) have been created from the wild-type W29 strain (Mličková et al. 2004a, 2004b). These strains were subjected to disruptions of the genes implicated in the encoding of various intracellular Aox. The genetically engineered strains, hence, either under-expressed or did not at all express several of the enzymes implicated in the catabolism  $(\beta$ -oxidation) of aliphatic chains. When cultures were performed on oleic acid utilized as the sole substrate, although the genetically engineered strains showed almost equivalent microbial growth compared with the wild strain (W29) from which they derived, in contrast with W29 strain they presented significantly higher formation of lipid bodies and, hence, increased lipid accumulation (Mličková et al. 2004a, 2004b). Therefore, the above-mentioned studies as well as various others reported in the literature (Aggelis and Sourdis, 1997; Papanikolaou et al., 2003; Szczesna-Antczak et al., 2006; Mantzouridou and Tsimidou, 2007) indicate that external addition of fat (ex novo lipid accumulation) can significantly enhance the bio-process of SCO production in various oleaginous microorganisms, but external utilization of fat mainly serves for the 'improvement' and 'upgrade' of a fatty material utilized as substrate [e.g. valorization of low-cost or waste fats so as to produce specialty lipids like cocoa-butter substitutes or substitutes of other

high-added value lipids like illipé butter, shea butter, sal fat (Papanikolaou and Aggelis, 2010)] and not for the use of the SCO produced in the manufacture of bio-diesel.

## 8.4 Biodiesel production from single cell oil

The conversion rate of TAGs to FAMEs, changes in the composition of biodiesel during transesterification and analysis of biodiesel characteristics are the main aspects that are investigated in most studies about biodiesel production from vegetable oils (Darnoko and Cheryan, 2000; Dorado *et al.*, 2004; Vicente *et al.*, 2005; Arzamendi *et al.*, 2006). The above parameters are related to the FAME concentration resulting during transesterification and characterize biodiesel yield or purity (Vicente *et al.*, 2007). Contrary to biodiesel production from vegetable oils, there are limited publications investigating the optimum conditions (e.g. reaction duration, reaction temperature, agitation, type and amount of catalyst, ratio of alcohol to SCO) for biodiesel production from SCO.

SCO derived from various yeast and fungi should be thoroughly compared with vegetable oils in order to justify the possibility to substitute for the current raw materials used for biodiesel production. SCO-derived biodiesel should be characterized according to biodiesel standards ASTMD 6751 (USA), DIN 51606 (Germany) and EN 14214 (European Organization). Preliminary results indicate that SCO could be regarded as a potential raw material for biodiesel production. Li *et al.* (2007) claimed that the fatty acid distribution of the SCO produced during fed-batch fermentations by *Rhodosporidium toruloides* could be converted into biodiesel with a cetane number (CN) higher than 51, which meet the minimal CN standards (47, 49 and 51) set by ASTMD 6751, DIN 51606 and EN 14214. Zhu *et al.* (2008) reported that the SCO produced by *T. fermentans* contained an unsaturated fatty acid content of 64% which is similar to that of vegetable oils but a relatively high acid value of 5.6 mg KOH/g. After pretreatment of SCO, transesterification via methanolysis resulted in a methyl ester yield of 92% (Zhu *et al.*, 2008).

Transesterification of SCO could be carried out either directly without extraction of SCO from the microbial biomass or indirectly after extraction of SCO from microbial cells. Extraction of SCO from cellular biomass components by solvent extraction or other means will increase production cost and capital investment. It is therefore evident that future research should investigate more thoroughly the direct transesterification of SCO without extraction from microbial cells. The processing steps of direct transesterification involves separation of cellular biomass by centrifugation after the end of fermentation, washing the cells with water, drying the cells to constant weight and finally mix the dry cells with a mineral acid solution (HCL or  $H_2SO_4$ ) and methanol (Liu and Zhao, 2007). Liu and Zhao (2007) reported that direct acid-catalyzed transesterification of SCO-rich microbial biomass from two yeast (*Lipomyces. starkeyi* and *R. toruloides*) and one fungal strain (*M. isabellina*) resulted in FAMEs with CN of 59.9, 63.5

and 56.4 respectively and lipid to FAME yields higher than 90% (w/w). The optimum reaction conditions applied by Liu and Zhao (2007) were 0.2 mol/L  $H_2SO_4$  at 70 °C for 20 h with a biomass-to-methanol ratio of 1:20 (w/v). Vicente *et al.* (2009) compared the efficiency of direct transesterification with indirect transesterification (lipid extraction was carried out by 3 solvent systems including chloroform:methanol, chloroform:methanol:water and n-hexane) for biodiesel production from SCO produced by the fungal strain *Mucor circinelloides*. The direct transesterification method produced FAMEs with higher purities (>99%) than those from the indirect process (91.4–98.0%) and a significantly higher yield due to a more efficient lipid extraction when the acid catalyst was present (Vicente *et al.*, 2009). The reaction conditions applied by Vicente *et al.* (2009) were 8% (w/w relatively to the microbial oil) BF<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or HCl for 8 h at 65 °C with a methanol to oil molar ratio of 60:1.

## 8.5 Future trends

Future research incentives on the development of biorefineries should focus on all aspects of the process regarding upstream processing (i.e. evaluation of various renewable raw materials and conversion strategies), bioconversion for SCO production, downstream conversion of SCO into biodiesel and generation of co-products through valorization of crude glycerol or other side/waste streams. Furthermore, it is essential to evaluate the economic viability and sustainability of industrial-scale SCO-based biodiesel production. In the 1980s, Davies (1992) reported the most thorough economic analysis for SCO production (\$0.8 - 1 per kg MO) from waste lactose ( $200000 \text{ m}^3$  whey per year) utilizing the yeast strain *Candida curvata*. Based on this cost and using an order-of-magnitude approximation, the SCO production cost in 2008 would have been \$1.4 and 1.8/kg (this value does not include the biodiesel production cost from SCO) in the case that whey is used as carbon source.

If we consider that biodiesel production from SCO is still at an early research stage, then the above economic considerations demonstrate that SCO production deserves more thorough research and development. For instance, maximization of SCO production would only be achieved by optimizing fed-batch fermentations due to the nature of SCO biosynthesis. In fed-batch bioconversions, a nutrient-complete feedstock could be provided in the first stage to achieve high microbial growth, while in the second stage we could provide a nitrogen limited medium that contains a high amount of a carbon source in order to promote SCO accumulation. Li *et al.* (2007) achieved 106.5 g/L total dry weight, 67.5% (w/w) SCO content and 0.54 g/(L.h) SCO productivity during fed-batch fermentations in a 15 L bioreactor. Meesters *et al.* (1996) employed a fed-batch fermentation process using glycerol as carbon source to produce high cell densities of 118 g/L with a lipid production rate of 0.59 g/(L.h) and a cellular lipid content of 25% (w/w). Higher total dry weights (185 g/L and 153 g/L) with reasonably high

lipid contents (40% and 54%, w/w) have been achieved in other studies employing fed-batch fermentations with the yeast strains *Rhodotorula glutinis* and *L. starkeyi*, respectively (Yamauchi *et al.*, 1983; Pan *et al.*, 1986). It should be stressed that a relatively low number of publications have been published in the literature regarding SCO production via fed-batch fermentations. Therefore, research should focus on the optimization of fed-batch bioconversions for SCO production. Furthermore, the application of genetic engineering and metabolic engineering to oleaginous microorganisms will lead to enhanced SCO production.

Previous studies on SCO production focus on the utilization of commercial nutrient supplements (e.g. yeast extract, inorganic chemicals) to formulate the fermentation medium. Li *et al.* (2007) reported that the utilization of commercial sources of glucose, inorganic salts and protein supplements result in a higher biodiesel production cost as compared to the cost of biodiesel production from vegetable oils. Future research should focus on the utilization of agro-industrial residues and wastes for the formulation of the required media for SCO fermentation. It was previously stressed that the addition of protein hydrolysates could enhance SCO accumulation by certain microorganisms.

Future research should also focus on the complete characterization of SCO as raw material for biodiesel production, including analysis of free-fatty acid composition, water content, acidity, peroxide value, density and kinematic viscosity. The efficiency of transesterification and the performance of biodiesel in diesel engines are strongly dependent on these properties. For instance, in the case that SCO or any other renewable source of oil has a high FFA content, the use of homogeneous acid catalysts rather than alkaline catalysts is recommended, because the utilization of alkaline catalysts will hinder separation and purification of the final product due to excessive soap formation. In addition, the selection of the most appropriate microorganism will be dependent on the quality of the SCO required for biodiesel production.

## 8.6 References

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# Biochemical production of bioethanol

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**Abstract:** Bioethanol can be produced from different sources of biomass including biological material from agricultural products and forest raw materials. The chapter first discusses the different biomass feedstock available for both first and second generation bioethanol production. It then discusses the various process technologies including pre-treatment, acid hydrolyses, enzymatic hydrolyses and fermentation steps to convert the various feedstock to bioethanol. The chapter includes a description of a pilot plant for production of bioethanol from lignocellulosic materials. Environmental aspects and future trends of bioethanol production have also been discussed.

**Key words:** biomass (lignocellulosic) feedstock, enzymatic hydrolyses, acid hydrolyses, bioethanol process tecnology, fermentation.

#### 9.1 Introduction

For many years transport systems have relied on fossil fuels such as petrol, diesel and natural gas but these fuels are not sustainable in the long term. Petroleum prices have increased steadily over recent years which has caused much interest and investment in biofuels production. Emissions of greenhouse gases such as  $CO_2$ ,  $CH_4$  and  $N_2O$  from the combustion of fossil fuels in the engines of motor vehicles have had negative impact on human health and also caused weather changes related to global warming. The Kyoto Protocol demands that the European Union cut  $CO_2$  emissions by 8% between 1990 and 2012. In 2007, the 27 European Union member governments approved a new target to cut their collective greenhouse gas emissions by 20% from the 1990 level by 2020.

The health and environmental problems together with increasing worldwide demands for energy and the depletion of fossil fuels in the near future call for sustainable production of fuels for the transport sector. At the same time, developing motor vehicles which increase efficiency and reduce fuel consumption has been urged. Therefore, the development of fuel systems that are based on renewable sources has been the topic of frequent international discussion.

Different transport fuels have different physical and chemical properties and they may exist as liquids or gases in many cases, e.g. biodiesel, biogas and bioethanol (ethanol derived from biological sources). The production of these from renewable resources has increased during recent decades. Liquid fuels are easily handled and possess a high energy content. The global production of bioethanol was 51 billion litres (13.5 billion gallons) in 2006 (Balat, Balat, and Öz, 2008; Sanchez and Cardona, 2008).

Bioethanol as a fuel has both advantages and disadvantages depending on the type of engine (Otto engine or diesel engine) using the fuel and there are some physical obstacles to bio-ethanol use. Bio-ethanol can be produced from different sources of biomass including biological material from agricultural products and forest raw materials, etc. The biomass feedstock can also be divided into several groups depending on the type of chemical structure of the raw material, e.g. sugar, starch or cellulosic materials. In a future bio refinery process the production of bioethanol should be integrated with the production of other value added chemical compounds and biofuels in order to be able to utilise the feedstock in an optimum way (Demirbas, 2009).

### 9.2 Properties

Ethanol, with the chemical formula  $C_2H_5OH$  is a colourless liquid with a boiling point of 78°C and has been used to large extent as a chemical compound in the medical and food industries. Ethanol is highly flammable and has a flame which is difficult to be seen. It is soluble in water and forms an azeotrope, so it is difficult to achieve 100% pure ethanol by distillation. Ethanol can be used as a pure fuel or blended with gasoline or diesel in a transport system. Ethanol has lower energy density (about 34% lower) and lower vapour pressure than gasoline which makes starts in cold weather difficult. Ethanol is less toxic than gasoline, diesel or methanol regarding safety and environmental issues. Ethanol can be broken down by bacteria to carbon dioxide and water and it can be produced from ethene obtained from fossil sources in oil refining and also from biomass as bioethanol.

The most important characteristic of ethanol which makes it suitable as a fuel for Otto engines is its high octane number. The octane number is a numeric representation of the anti-knock properties of a motor fuel. By definition, the octane number is zero for n-heptane and 100 for *iso*-octane (2,2,4-trimethyl pentane) and for other fuels the octane number is decided by comparison with a mixture of these two compounds. Liquid fuels with a high octane number have better properties during engine combustion. For ethanol, with a high octane number (129), it is possible to push more fuel-air mixture into the engine's cylinders (higher compression ratio gives higher efficiency and less fuel consumption) without any risk of uncontrolled self-ignition which may cause 'knocking' and serious damage to the engine as a consequence.

One disadvantage of ethanol is its low cetane number (8) and it can be used in diesel engines only if some ignition improver (e.g. di-tert-butyl-peroxides) is added to it. These kinds of additives are often costly, but there are commercially feasible alternatives in the market. The cetane number is a numeric representation of a fuel's ignition properties. By definition the cetane number is 15 for heptamethyl-nonane and 100 for n-hexadecane. For other fuels, it is decided by

comparison with a mixture of those two compounds. Too low a cetane number causes slow ignition and poor engine performance.

It is technically possible to add at least 10% bioethanol to gasoline without any need for changes in the engine of cars and this can reduce gasoline consumption and the net concentration of fossil  $CO_2$  in the atmosphere worldwide. One obstacle to mixing a higher percentage of ethanol in gasoline (petrol) is that car manufactures, in many cases, do not guarantee, for ethanol blends more than 5–10%, cars with ordinary gasoline engines. Several modifications are needed to minimise the risk of any damage to some parts of the engine if higher blends are used.

It is possible to use neat ethanol (99% pure, water free) or blended with petrol or diesel in Otto engines and diesel engines, respectively. There are two types of vehicles: one is the flexible fuel vehicle (FFV) in which it is possible to use up to 85% ethanol in petrol, the second group is the vehicles that use pure (neat) ethanol.

When it comes to blends, bioethanol with diesel in private cars or heavy vehicles (buses, trucks, etc), and the addition of emulsifying agents is essential to achieve a homogenous emulsion of ethanol and diesel (aliphatic hydrocarbons). In pure ethanol fuel for a diesel engine, addition of an ignition improver is necessary. The ignition improver will increase the production cost of the bioethanol as fuel in transport sector.

All bioethanol may not be used as transport fuel. In fact, ethanol is used in the production of other industrial chemical compounds such as ethylene, ethyl acetate, acetic acid and acetaldehyde by various chemical reactions, e.g. oxidation, esterification. Therefore, as the production of bioethanol increases, it will replace fossil sources for ethanol production in many aspects.

## 9.3 Feedstocks

The various biomass feedstocks that can be used for bioethanol production are divided into two major groups: first generation feedstocks and second (next) generation feedstocks. First generation feedstocks include sugar, sugar cane, sugar beet and starch crops like corn, wheat and barley. To the next generation feedstocks belong wood, grasses, forestry residues and other lignocellulosic materials as new, more sophisticated conversion technologies are developed to enable the production of bioethanol from cellulosic feedstocks. However, feedstock availability for ethanol production can be limited in some countries with low biomass resources, e.g. woody biomass resources in Finland and Sweden are huge however the woody biomass has been used in many ways such as fuel pellet production for combustion and electricity production and lignocellulosic materials have been used for many years in paper mills. In fact, the price of the feedstock is about one-third the cost of bioethanol production (Balat, Balat, and Öz, 2008) depending on feedstock. In addition, there are other aspects of feedstock production that should be considered such as national and international regulations and policies, environmental questions, protection of high-value habitats and competition between food production and biofuel feedstock. It is also important to be able to determine the chemical composition of a feedstock (i.e. sugar units, extractives, lignin, etc.) by fast and non-destructive methods such as near infrared spectroscopy (NIR; Sanderson, Agblevor, Collins, and Johns, 1996).

There are three different groups of feedstocks available for ethanol production: sugar feedstock such as sugarcane and sugar beet; starch feedstock such as cereal grains and potatoes; and cellulose feedstock such as forest products and agricultural residues. In general, the sucrose-containing materials such as sugarcane allow the production of ethanol for the lowest costs compared to the starchy materials and lignocellulosic feedstocks.

## 9.3.1 Glucose (sucrose) feedstock

Sugarcane production requires a tropical climate and Brazil has the largest sugarcane cultivation (about 27% of global production) and was the first and biggest producer of bioethanol in the world for many years. Sugarcane (*Saccharum* spp.) contains about 15% sucrose (saccharose) which is a disaccharide of hexose units (one molecule of glucose and one molecule of fructose). The chemical bonds can be broken relatively easily (e.g. by yeast *Saccharomyces cerevisiae*) resulting in glucose which is free and available for fermentation in the ethanol production process. The sucrose is extracted from the sugarcane by pressing the already chopped and shredded cane. The remaining solid biomass from the pressing (bagasse) is fibrous and usually used as a fuel in the sugar mill. Several steps are involved in isolating sugar as a pure solid, including several crystallisation steps, however these purification steps are not necessary in ethanol production. The sugarcane must be processed a short time after harvesting (normally within 48 hours of harvesting) to achieve the maximum yield of ethanol avoiding the possible oxidation and degradation of the sugar units.

Sugar beet (*Beta vulgaris* L.) is a plant whose roots contain large amount of sucrose (about 17%). Sugar beet generates good yields (more than 50 tonnes/ha) but compared to sugarcane is an energy- and chemical-intensive crop. Sugar beet cannot be cultivated more than once every three years on the same field because of the potential survival of pests in the soil. After the washing of sugar beet, the beet is sliced, pressed and the sugar content separated from water by several decolourisation and separation techniques. Mostly, European countries like France and Russia together with the USA produce most of the sugar beet in the world, e.g. the ten biggest producer countries in Europe produced 242 million metric tons of sugar beet in 2005.

# 9.3.2 Starch crops (feedstock)

Bioethanol production can use starch rich crops such as corn, wheat, barley, potato and also cassava. The second largest feedstock for bioethanol production is corn



9.1 Structure of starch.

(known also as maize) which has been widely used in the USA. Wheat and sugar beet are dominant feedstocks in Europe. Starch is a polymer of glucose molecules connected to each other by glycosidic bonds ( $\alpha$ 1,4-glycosidic) forming a long chain, the structure of starch, for example amylose, is shown in Fig. 9.1. The  $\alpha$ -bond gives the starch polymer a helical shape which makes it unable to form stabilising hydrogen bonds between the starch molecules.

Ethanol production from cereal grains such as corn, wheat and barley requires additional processing steps for conversion of the feedstock to sugar units compared to sugarcane and sugar beet. The process starts with the milling of the grains and then with hydrolysis of the starch polymers to sugar units. The other steps in the process are similar to those of other feedstocks normally used for bioethanol production. For example, the starch in corn is converted to glucose after grinding in a dry mill, reacted with dilute acid and then reacted with amylases, e.g.  $\alpha$ -amylase and glucoamylase. The fermentation and distillation steps are similar to those used in bioethanol production from sugarcane.

Cassava (*Manihot esculenta* spp. *esculenta*) is a starch rich root crop that can be used for bioethanol production. Mostly cassava, until now, has been used in the food industry and as an animal feed because of its high content of starch. The production yield is around 20 tonnes/ha. Cassava can be cultivated in tropical and subtropical regions, i.e. in Africa, some parts of Asia (Thailand, China about 400 000 ha) and Latin America. The yield of anhydrous ethanol varies depending on starch content of the roots but is around 200 litre/tonne of cassava roots, in other words around 6.6 tonnes of cassava roots are needed for the production of one tonne of bioethanol (Jansson, Westerbergh, Zhang, Hu, and Sun, 2009). In addition to cassava roots, the stem and leaves (fibrous parts) of the cassava plant can be collected and used as a lignocellulosic feedstock for ethanol production.

#### 9.3.3 Lignocellulosic feedstock

There is a vast amount of lignocellulosic waste material from agriculture and the forest industry which can be used for ethanol production. Lignocellulosic biomass like wood and fast growing plants like switch grass, reed canary grass or crop

residues from food production such as corn stover are cellulose feedstocks which can be used in bioethanol production.

Lignocellulosic biomass is composed of polymeric structures of cellulose, hemicellulose, lignin, other organic compounds (extractives) and inorganic salts. Cellulose is the major component in most lignocellulosic biomass. In fact, it is the most abundant polymer on earth. Like starch, cellulose is a polymer of glucose molecules and the chain length varies between 100 and 14000 units. However, in cellulose the glucose units are connected to each other by  $\beta$ –1,4-glycosidic bonds instead of  $\alpha$ –1,4-bonds as in starch, the structure of cellulose is shown in Fig. 9.2.

This makes a crucial difference compared to starch. In cellulose the glucose polymer is linear giving the possibility for the cellulose chains to align with each other and form multiple hydrogen bonds between the chains. In this way, cellulose can form crystalline structures. These crystalline structures are very stable and they are the reason why it is so difficult to hydrolyse cellulose: the crystals are so tight that it is very difficult for the hydrogen ions and the water that is needed for the hydrolysis to actually get to the glycosidic bonds. In fact, although cellulose consists of very polar glucose units, the tight hydrogen bonds prevent water solvating the polymer and therefore cellulose is not soluble in water. This is fortunate because otherwise cotton clothes (cotton being pure cellulose) could not be washed and would not be so useful! However, not the whole portion of cellulose is in the crystalline form, in some locations, the crystal structure is disturbed and an amorphous form of cellulose is formed. This form is not as stable as the crystalline form and is more susceptible to hydrolysis.

The cellulose chains that are held together with hydrogen bonds form what are called fibrils and a bundle of these fibrils then forms the actual cellulose fibre. In order to 'soften' the cellulose, the hydrogen bonds must be broken and that is why the concentrated acid method is so effective: in such a high concentration of acid or also in fact strong base, the hydrogen bonds are broken and access to the glycosidic bonds is made. The double sugar units with a  $\beta$ -1,4-bond between the two glucose units is called cellobiose.

Hemicellulose is a branched polymer of both 6-carbon sugars (hexoses) like glucose, mannose and also 5-carbon sugars (pentoses) like xylose. In grasses and hardwoods, the pentoses in the form of xylans dominate, while in softwoods the major hemicellulose component is the hexosic glucomannan. Since the hemicellulose polymer chain is branched, the formation of hydrogen bonds creating the crystalline



9.2 Structure of cellulose.

structure of cellulose is prevented. This makes hemicellulose much more susceptible to the hydrolysis of the glycosidic bond. Actually, hemicellulose in solution is as easy to hydrolyse as starch. Two different structures of hemi-cellulose are shown in Fig. 9.3.

Lignin is a polymeric structure of aromatic units (p-hydroxy-phenyl-propanoid units) and the second most prevalent polymer on earth. Lignin functions as the glue between the cellulose fibres in the lignocellulosic biomass. The amount of lignin varies depending on the type of biomass; Table 9.1 shows the typical composition of cellulose, hemicellulose and lignin in different types of biomass.

The composition of lignin also varies between different types of biomass. The phenyl ring in the monomer structure of lignin can either have no, one or two



9.3 Two hemicellulose structures: xylan and glucomannan.

Feedstock	Glucan	Xylan	Arabinan	Galactan	Mannan	Klason lignin	Extractives
Spruce	41.4	4.7	1.9	2.0	11.5	24.6	5.3
Pine	41.7	4.5	1.8	2.2	11.1	24.8	6.7
Birch	40.7	20.0	0.6	0.7	1.7	19.5	4.1
Aspen	43.2	15.1	0.8	0.5	2.2	16.0	4.7
Willow	33.1	10.3	1.4	1.4	1.6	23.4	7.7
Wheat straw	38.8	19.6	2.7	0.8	0.3	19.0	4.8
Corn stover	40.4	17.5	3.0	1.1	0.3	17.2	7.8
Reed canary grass	43.0	19.0	2.0	0.3	0.1	17.9	3.7

*Table 9.1* Per cent dry weight compositions of different feedstocks analysed at SLU laboratory in Umeå, Sweden

methoxy groups. In grasses the non-methoxy monomer is predominant, in hardwoods there is a mix of all three and in softwoods the one and two methoxy rings are predominant. Since lignin does not contain as much oxygen as cellulose and hemicellulose, the energy value is much higher. Cellulose and hemicellulose have an energy value (calorific value) of approximately 17 MJ/kg, while lignin has up to 25 MJ/kg. So although lignin is only around 25% of the dry solid content in wood for example, almost 40% of the heat value comes from it. A structure of a segment of lignin in softwood is shown in Fig. 9.4.

Historically, lignin has always been utilised as an energy source, for example in the energy recovery boilers of the pulp and paper industry. In a future bio-refinery process lignin may have a more important role as a feedstock for the production of several organic compounds, e.g. phenol. One problem chemically with lignin produced in a dilute acid or enzymatic process is that it is highly condensed which reduces the number of reactive hydroxyl groups and therefore there are problems to react it further.

Switch grass (*Panicum virgatum* L.) is a perennial warm-season  $C_4$  species (tolerant to heat and cold), which can be used in bioethanol production. This grass



9.4 Structure of lignin.

is grown in Central USA as a fodder crop or for soil conservation and is a potential long-term bioethanol feedstock to replace corn. The composition of switch grass on a dry basis is about 30–36% cellulose, 24–27% hemicellulose and 16–18% lignin. From highly adapted switch grass varieties the theoretical ethanol production potential is about 5000–6000 litre/ha. Based on the technique used in ethanol production the ethanol yield is often high (72–92% of the theoretical value in labscale). The excess of switch grass can be used to produce Kraft pulp with short fibres (Keshwani and Cheng, 2009).

Reed canary grass (Phalaris arundinacea L.) is a perennial rhizomatous grass which is mainly used as a raw material for solid biofuel production in the Nordic countries. This grass grows naturally in Europe, Asia and North America, especially in wet and humus rich soil. The grass is about two meters tall with a sturdy, upright straw, broad leaves and a long panicle. The annual production yield is eight to ten tonnes dry solid/ha in Sweden (Xiong, Landström, and Olsson, 2009). The harvesting starts normally some years after establishment and growth persists for at least 12 years (Xiong, Landström, and Olsson, 2009). The grass is usually stored and transported as bales to increase the density and reduce production costs. Reed canary grass consists mainly of cellulose, hemicellulose and lignin, but there are also proteins, lipids and a relatively high content of inorganic material. The main sugars after hydrolysis of reed canary grass are glucose, xylose and also arabinose. In reed canary grass, the amount of hexoses in the stem varies between 38% and 45% of the dry weight of the material and the amount of pentoses about 22-25%. The lignin content varies between 18% and 21% of the dry weight. Therefore, the grass has a good potential as a feedstock for ethanol production in the future (Arshadi and Sellstedt, 2008).

Reed canary grass has also been found to be a useful complement to short fibre raw materials like birch in kraft pulp production (Paavilainen, 1996; Finell and Nilsson, 2004). Alfalfa (*Medicago sativa* L.) is usually used for the production of fuel, feed and other industrial materials. Alfalfa stems consist mainly of cellulose, hemicellulose, lignin, pectin and proteins. Therefore, the feedstock has the potential to be used for ethanol production and also other chemicals (Diena *et al.*, 2006).

Previous work has shown that it is possible to produce ethanol from alfalfa either by separate hydrolysis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF). The yield of fermentable sugars from hydrolysis or saccharification is an important response variable in assessing the value of the feedstock. Corn seed has been used as a starchy feedstock in bioethanol production but other parts of the corn plant have not been used until recently. The stalk and the leaves, which are called corn stover, can be used as a source of lignocellulosic material in ethanol production; also the corn cob can be used. The amount of corn stover is huge since for every kilogramme of produced corn, almost the same amount of corn stover is left. The amount of corn stover available for fermentation usage is estimated to be between 60 and 80 million dry tonnes per year (Kadam and McMillan, 2003). Some of the corn stover needs to be left in

the field to prevent soil erosion and also corn stover may be needed as a feedstock for bio-based materials like composite products (Kadam and McMillan, 2003), but some part can be collected and used as a raw material in bioethanol production (Öhgren, Rudolf, Galbe, and Zacchi, 2006).

Rice straw is another lignocellulosic material that can be used as a raw material in bioethanol production, the annual world production of which is about 731 million tonnes. This amount of biomass has the potential to produce 205 billion litre of bioethanol (Balat, Balat, and Öz, 2008). Actually, the use of rice straw as a feedstock for bioethanol production will increase the income of farmers in many places with a gain in rice production which is an important carbohydrate source for many people in the world.

Sawdust and wood chips from softwoods (pine, spruce) are another important feedstock for ethanol production. Until now most of the excess of sawdust in some countries (e.g. Sweden, Finland) has been used as a raw material for wood pellets, a solid biofuel, for heating. The annual amount of sawdust used for the production of wood pellets is more than three million tonnes in Sweden alone. In fact the wood pellets production in North America has been increased drastically in recent years. However, for sustainable usage of the forest resources in a future bio-refinery, the extractives from the biomass can be extracted for the production of chemicals, with then the possibility of releasing the cellulose and hemicellulose components and converting them to ethanol. The residual, which contains mostly lignin together with additional sawdust and other biomass, can still be used as a feedstock for the wood pellet industry.

# 9.4 Processing technology

Historically, the production of ethanol was developed thousand years ago when it was produced as wine from grapes. Ethanol was also produced from grains. For many years ethanol has been produced by the catalytic addition reaction of water to ethene which is a fraction from oil refining. But a sustainable ethanol production needs renewable raw materials (feedstock) and cost-efficient methods to be able to replace ethanol made from a fossil precursor. There are some differences in the processing technology between first generation feedstocks (sugar feedstock, starchy feedstock) and second generation feedstocks (lignocellulosic feedstock).

Generally, commercial bioethanol production requires several steps:

- Preparation of the feedstock to achieve maximum yield of the feedstock and also its sugar content.
- Preparation (actually size reduction) of the feedstock to achieve the right (optimal) physical size and form of the raw material in the ethanol production process. This also reduces the transport cost of the feedstock.
- Pre-treatment of the feedstock to release cellulose, starch or sucrose from lignin, fibre and other biological parts of the raw material.

- Hydrolysis of the feedstock to achieve partial or complete hydrolysis of the simple and complex polymeric molecules to produce sugar units. This hydrolysis might be either thermochemical hydrolysis or a combination of thermochemical and biochemical hydrolysis.
- Fermentation of the sugar units from the hexose fraction to ethanol by yeast.
- Fermentation of the sugar units from the pentose fraction to ethanol by other microorganism or enzymes.
- Several purification and distillation steps.

A schematic figure of different steps in bioethanol production is shown in Fig. 9.5.



 $9.5\,$  Scheme of different steps in bioethanol production from different feedstocks.

Preparation of the feedstock is an important part of ethanol production since a substantial part of the ethanol production cost is the price of the feedstock, depending on what feedstock is used. Therefore, it is essential to optimise the yield of the feedstock with a high amount of fermentable sugar content. Preparation of the first generation feedstock usually includes cutting the material to proper size and form, e.g. sugarcane chopped and milled (dry or wet milling) and corn or woody materials chopped as chips. An optimum size of the feedstock reduces the transport cost and thereby production cost of bioethanol. Size reduction also increases the contact surface of the feedstock with the pre-treatment catalysts.

In the pre-treatment, the raw material is subjected to a mechanical or thermochemical treatment to make the carbohydrate polymers (cellulose and hemicellulose) available for hydrolysis. In the hydrolysis process, the polymers are hydrolysed into fermentable sugar units. Depolymerisation of lignocellulosic feedstock releases both pentoses and hexoses, depending on what type of feedstock is used. When the sugars have been released, fermentation takes place. The fermentation is an anaerobic catabolism of sugar by one or several microorganisms. After the fermentation step the ethanol concentration varies between 4% and 15% depending on what kind of feedstock is used (first or second generation) and what process. The ethanol is then purified by filtration and/or distillation steps. The ethanol concentration is increased to a maximum of 95% after distillation and after the absolutisation (drying) step it is more than 99% pure ethanol. The distillation and absolutisation steps require lots of energy. There are both similarities and differences between ethanol production techniques using first generation feedstocks and second generation feedstocks, and therefore the processing technology for ethanol production is separated into different sections.

# 9.4.1 Technology for conversion of first generation feedstock

Pure sugar is relatively easily converted to ethanol by a biochemical pathway (fermentation) in several steps. Production of a sugar solution from sugarcane and/or sugar beet is quite straightforward since fermentable carbohydrates can be obtained just by extracting the raw material with water. In the case of starch-based raw material, the process becomes a little bit more complicated. The fermenting organisms need mono- or disaccharides to produce ethanol, and since starch is a polymer, the fermentation rate is very slow. In order to increase the rate, the polymer has to be broken down into monomers. The polymeric starch in wheat or corn is stored in granules. When the granules are heated in water, the hydrogen bonds between the polymer chains are broken and a water solution of starch is formed. To this solution, enzymes called amylases and amyloglucosidases are added. These enzymes then hydrolyse the glycosidic bonds between the monomers which results in a solution of fermentable monomers. The amylases randomly cut the bond between two sugar units, reducing the chain length, while the

amyloglucosidase peels off one sugar unit at a time from the ends of the chains. By themselves, these enzymes are very inefficient in cleaving the starch polymer into monomers, but working together (synergic effect) gives a very efficient hydrolysis.

#### Fermentation

After the pre-treatment and the degradation stage that releases the sugar units it is possible to convert the carbohydrates to ethanol by the technique of fermentation. Baker's yeast (*Saccharomyces*) is most commonly used and is able to convert glucose to ethanol under both aerobic and anaerobic conditions. During the fermentation process, two moles of carbon dioxide and two moles of ethanol are produced from one mole of a sugar unit. In order to achieve optimal fermentation there are several characteristics of the fermenting microorganisms that should be considered, e.g. temperature range, pH range (3.5–5.0 for yeast, 6.5–7.0 for bacteria), alcohol tolerance, growth rate, genetic stability, inhibitor tolerance, yield, etc. (Bai, Anderson, and Moo-Young, 2008). The fermentation process can occur either in separate batches or as a continuous process which is often more preferable economically (Sanchez and Cardona, 2008).

#### Distillation and purification

During the fermentation process it is important to separate the produced ethanol from the original liquid since several microorganisms are not able to survive the high concentration of ethanol (more than 15–20%). The remaining liquid contains ethanol and water (about 80%) and other soluble compounds and ethanol can be separated by distillation or supercritical fluid technology (Schacht, Zetzl, and Brunner, 2008). Unfortunately the distillation requires a lot of energy to obtain 95.6% ethanol (azeotrope mixture of ethanol and water). In the next step the ethanol is further purified (99%) by adding a drying agent to the solution or by molecular sieve adsorption. But the 99% ig (industrial grade) ethanol is hygroscopic and may absorb water again from the surrounding air during storage. The purification (i.e. dehydration) steps are necessary since the ethanol/gasoline blend will separate in the presence of water and is difficult to remix (Szulczyk, McCarl, and Cornforth, 2010).

# 9.4.2 Technology for conversion of second generation feedstock

Lignocellulosic feedstocks are often more difficult to break down into their constituent parts in comparison with first generation feedstocks. Therefore, the conversion technologies are also more costly. A schematic diagram of a potential ethanol production process from cellulosic feedstock is shown in Fig. 9.6.



9.6 Scheme of bioethanol production from lignocellulosic feedstock.

The lignocellulosic feedstock after collection is too bulky and needs to be converted to an optimal size by mechanical steps like chipping, grinding and milling. These size reduction steps are necessary to achieve an optimal size of the feedstock.

#### Pre-treatment technologies

The cellulose and hemicellulose part of lignocellulosic feedstock needs to be detached from the lignin part and this is possible either by physical and/or chemical and/or biological pre-treatment. In the physical pre-treatment technique no chemicals are involved. Physical pre-treatments can include: communition i.e. dry, wet and vibratory ball milling; irradiation i.e. electron beam irradiation, or microwave heating and also steam explosion (Wyman, 1996).

In the irradiation pre-treatment method electron beam irradiation or microwave assisted depolymerisation are used to separate cellulose or hemicelluloses from lignin. Electron beam irradiation has some effect on fatty and resin acids in the wood material and changes the physical properties of sawdust (Finell, Arshadi, Gref, Knolle, and Lestander, 2009). However, the irradiation pre-treatment method for ethanol production is not commercial.

In the physical steam explosion pre-treatment, the chipped lignocellulosic materials such as hardwood is treated by high pressure saturated steam (autohydrolyses) and then by reducing the pressure quickly, the material undergoes an explosive decompression. This results in hemicellulose degradation and some changes in polymeric lignin structure with the cellulose becoming more accessible for hydrolysis.

The addition of dilute acid in the steam explosion method (so-called acid catalysed steam explosion) may improve enzymatic hydrolysis of the cellulose and facilitate removal of the hemicellulose. Steam explosion requires less energy than mechanical pre-treatment methods (communition) and is the most effective pre-treatment method for hardwoods and agricultural lignocellulosic products. One disadvantage of the steam explosion pre-treatment method is the formation of some inhibitory compounds for enzymatic hydrolysis in the next step in ethanol production (Sun and Cheng, 2002).

There are other physical-chemical pre-treatment methods such as ammonia fibre explosion (AFEX) where lignocellulosic feedstock is exposed to liquid ammonia at high temperature and pressure over a period of time and then the pressure suddenly lowered. This method can be used for many different materials including corn stover, wheat straw, softwood newspaper, switch grass, alfalfa, etc. In contrast to acid catalysis steam explosion, the AFEX pre-treatment does not significantly solubilise hemicellulose and high hydrolysis of hemicellulose and cellulose has been obtained after this pre-treatment method. But the superheated ammonia vapour must be recovered to protect the environment (Sun and Cheng, 2002).

In the chemical pre-treatment method some chemical/s are added to the feedstock, e.g. concentrated acids, dilute acids, alkaline solutions. It is possible to use concentrated acids such as  $H_2SO_4$  and HCl for pre-treatment (acid hydrolysis) of lignocellulosic feedstock. The acids effectively hydrolyse the cellulose. However the concentrated acids are toxic, corrosive and must be recovered after the process. Therefore, dilute acid hydrolysis (e.g. sulphuric acid, hydrochloric acid) as a pre-treatment has been used instead in many applications (softwoods, hardwoods, agricultural residues) with a high reaction rate and effective cellulose hydrolysis. But a neutral pH is necessary for enzymatic hydrolysis or fermentation. One advantage of dilute acid hydrolysis as a pre-treatment method in comparison to the steam explosion method is that the xyloses in hemicellulose remain intact with high yields (Wyman, 1996). These xylans can be utilised in value-added products.

Alkaline pre-treatment with sodium hydroxide alone or in combination with other chemicals like peroxide are most effective for agricultural residues rather than wood feedstock. By this method the lignin is effectively removed and some of the hemicellulose solubilised as well (Wyman, 1996). In the biological pre-treatment technique, microorganisms degrade the lignin (lignin solubilising microorganism) by producing lignin-degrading enzymes and no chemicals are needed. The method is slow which makes it less economical and sometimes consumes hemicellulose as well but it does not require a high energy input and only needs mild environmental conditions (Wyman, 1996).

Recently, Lignol Innovations Corporation has developed a method based on an ethanol-based organosolv pretreatment (i.e. delignification by extraction of lignin from the lignocellulosic biomass with organic solvents or their aqueous solutions) to separate lignin, hemicellulose components (e.g. xylose) and extractives from the cellulose part of the woody biomass (Arato, Kendall, and Gjennestad, 2005). In a review article the prospects and evaluation of different organosolv methods and mechanisms have been presented recently (Zhao, Cheng, and Liu, 2009)

In general, an optimal pre-treatment stage should improve the enzyme/ hydrolysis accessibility, should avoid the degradation of carbohydrates and should avoid the formation of by-products which may have inhibitory effects on the hydrolysis and fermentation steps. In another words, any pre-treatment method must be tailored to the specific lignocellulosic material with different chemical and structural compositions. The economic aspects are also very important in large scale industrial bio-ethanol production.

#### Hydrolysis technologies

During hydrolysis, water molecules react with the glycosidic bonds in the structure of cellulose and hemicellulose and degrade them to sugar units such as glucose, xylose, etc. Free sugar units can be obtained from lignocellulosic material by either thermochemical processes or a combination of thermochemical and biochemical processes.

The chemical processes are divided into two general types, one using high acid concentration in the hydrolysis step, one example is called the Concentrated Hydrochloride Acid Process (CHAP), and one using dilute acid in the hydrolysis step, one example was developed in cooperation between Canada, America and Sweden (called CASH).

#### **CHAP** process

The Concentrated Hydrochloride Acid Process (CHAP) is based on the hydrolysis of lignocellulosic feedstock by concentrated hydrochloric acid at low temperature. The process was developed for cellulose rich raw material since a high concentration of the acid may cause the degradation of pentose in hemicellulose to furfural derivatives. The ethanol yield is typically about 35%. The concentrated acid is corrosive and the process needs higher capital investment due to more expensive materials. The dangers associated with the recovery of the concentrated acid make this method less attractive. In addition, during combustion of lignin which is contaminated with hydrochloric acid there is some risk for dioxin emissions. Due to the corrosive problems with hydrochloric acid, focus has moved to concentrated sulphuric acid however, the major problem of recovering the acid remains unsolved so far.

#### **CASH** process

The Canada, America and Sweden Hydrolysis (CASH) process was developed in cooperation between Canada, America and Sweden. In this method, hydrolysis occurs with dilute sulphuric acid at a temperature of around 200°C (pressure 8–25 bar). Previous studies have shown that by using SO<sub>2</sub> and dilute sulphuric acid in two steps, this increases the sugar and also ethanol yield since the amounts of inhibitors such as furfural are decreased. The process was developed for woody biomass. The ethanol yield is around 20% of the energy content in the raw

material, however, up to 40% of the energy content of the biomass is bound in the hydrolysis residue, mostly the insoluble and condensed lignin, but also a large portion of unreacted cellulose. The reason why there is cellulose left in the hydrolysis residue is due to the reaction kinetics of the hydrolysis compared to the kinetics of the sugar break down reactions. At the end of the reaction, only the very stable form of the cellulose is left, making the hydrolysis reaction very slow, but at the same time, the sugar concentration has increased, making the breakdown reactions faster. At one point, the breakdown of the carbohydrates is faster than their formation and thereby the sugar concentration declines. The hydrolysis residue can be used as a solid biofuel in boilers or directly in powder fuel turbines or pelletised.

#### **Enzymatic hydrolysis**

In enzymatic hydrolysis the cellulose structure is selectively converted to glucose by enzymes. The biomass has to be pre-treated, e.g. with a short, dilute acid hydrolysis step in which the structure of the cellulose is disrupted and the hemicellulose is broken down into fermentable sugars. The cellulose is then broken down by cellulases into cellobios which in turn is cleaved by  $\beta$ -glucosidase into glucose. The sugar losses are minimal and the amount of by-products is negligible. An optimal enzyme activity and optimal reaction conditions such as temperature (45–50°C) and pH (4.8) will increase the ethanol yield. An optimal amount of substrate has a positive effect on the reaction rate and sugar yield as well. There are two types of enzymatic hydrolysis: SHF and SSF. There are benefits and drawbacks with both methods, however, the enzymatic hydrolysis method is considered the best method to date of producing ethanol from biomass.

SHF: In the SHF method the pre-treated material is neutralised and subjected to the enzymatic activity of the cellobios and  $\beta$ -glucosidase. After the hydrolysis has stopped, the solid material is filtered off and the hydrolysate is fermented and then distilled. The major drawback of this method is that the enzyme activity is inhibited by the product of its work: cellobios and glucose. This means that the sugar concentration is limited to approximately 6%, giving a maximum theoretical ethanol concentration after fermentation of 3%. This is not economically viable because the cost of distillation increases dramatically when the ethanol concentration drops below 4%. The benefit is that the temperature during hydrolysis can be kept at an optimal level and that the yeast cells can be recovered after fermentation.

*SSF*: To solve the problem of the low concentration of ethanol in SHF, SSF mixes the pre-treated material with both enzymes and yeast. This means that as soon as glucose is formed, the yeast will consume it and produce ethanol. The result is that the enzymes never 'sense' a high glucose or cellobiose concentration giving a higher ethanol concentration. The major drawback is that during hydrolysis the temperature must be held at 35°C due to the presence of the yeast

cells, slowing the hydrolysis down and the yeast cells cannot be recovered. Since there is solid material together with the yeast cells neither centrifugation nor filtration is an option for separating the yeast for recovery. Both processes have common drawbacks also: first enzymatic hydrolysis is relatively slow compared to a thermochemical process. This means that the reaction vessels in a large scale production unit will be very large with challenges with agitation and temperature control. Secondly the enzymes are presently too expensive to make the process economically viable. However, it is generally agreed that the cost of the enzymes will drop drastically when large scale production has started. Cellulase can be produced by fungi and bacteria under aerobic and anaerobic conditions and the microorganisms can be both mesophilic or thermophilic. The cellulase can be recovered after the reaction which will improve the yield of the hydrolysis and reduce the enzyme cost (Balat, Balat, and Öz, 2008; Sun and Cheng, 2002).

#### Fermentation

After the hydrolysis stage which releases the sugar units it is possible to convert the carbohydrates to ethanol by fermentation. Lignocellulosic fermentation is more difficult than glucose/starch fermentation since both the pentoses and hexoses should be converted to ethanol. *Zymomonas mobilis* is an anaerobic bacterium which can convert D-glucose, D-fructose and sucrose to ethanol. But Baker's yeast (*Saccharomyces*) is the most common agent and is able to convert hexoses like glucose to ethanol both under aerobic and anaerobic conditions. But ordinary Baker's yeast lacks the ability to convert pentoses like xylose to ethanol and other microorganisms are needed for that purpose.

During the fermentation process two moles of carbon dioxide and two moles of ethanol are produced from one mole of sugar unit. Today there are several xylose (pentose)-fermenting microorganisms (bacteria, yeast and fungi) available as native or genetically engineered organisms.

#### Distillation and purification

During the fermentation process it is important to separate the produced ethanol from the original liquid since several microorganisms may not survive the high concentration of ethanol (more than 15–20%). It is also necessary to separate the solid residue (including lignin, etc.) from the liquid mixture by for example filtration or centrifuging. The remaining liquid contains ethanol and water (about 80%) and other soluble compounds and ethanol can be separated by distillation or supercritical fluid technology (Schacht, Zetzl, and Brunner, 2008). During bioethanol production some by-products such as  $CO_2$ , furfural, etc. become available which can increase the incomes from/of bioethanol production to some extent. It is also possible to use the organic material that is left in the distillation residue in a bio treatment plant to produce biogas.

## 9.5 Pilot plant for ethanol production from lignocellulosic feedstock

For many years the research on bioethanol production was based on laboratory scale experiments but since the demand for commercial bioethanol production from lignocellulosic feedstock it has become necessary to use and test the present knowledge of the process of ethanol production on a larger scale; a pilot scale (100 times larger scale than laboratory scale) before it can be applied on a large industrial scale (100 times pilot scale) production. There are several practical and technical challenges that need to be solved before industrial scale bioethanol production can be established. A continuously operated pilot plant for ethanol production from lignocellulosic feedstock was inaugurated in Sweden in May 2004. It is a complete pilot plant from a raw-material intake of wood chips in truck carried containers to a distillation column producing ethanol with a concentration up to 94%. In between, there are stages for rinsing the wood chips, steaming, impregnation, digesting, filtration and fermentation. The pilot plant is operated 24 h/day, 7 days a week and processes up to 2000 kg of dry raw material producing up to 400 litre of ethanol/day. The reactor system is continuously operated and at high pressures. This means that the wood chips have to be transported from atmospheric pressure in the raw material intake to the pressurised reactors without interrupting the material flow.

The feedstock in this plant is spruce wood chips at the moment but other feedstocks such as bagasse and other agro-based feedstock will be tested in the future. The pilot plant has two thermo-chemical reactors giving the possibility to either perform a two-stage dilute acid hydrolysis or a pre-treatment for enzymatic hydrolysis. In the plant, possibilities for both SHF and SFF are available. Also, recycling of liquids is possible in order to reduce the amount of fresh water usage. Fermentation and enzymatic hydrolysis is performed in five bioreactors with the size of 10m<sup>3</sup>. A flow chart of possible steps in bio-ethanol production from lignocellulosic feedstock shown in Fig. 9.7.

# 9.6 Environmental aspects of ethanol as a biofuel

There is no doubt that combustion of fossil fuel in motor vehicles releases huge amounts of gases that can have a negative impact on human health and will change global climate drastically. Bioethanol as a fuel has the potential to lower emissions of harmful substances. The CO<sub>2</sub> emissions from the combustion of bioethanol from biomass will be consumed by plants during photosynthesis and the net introduction of CO<sub>2</sub> to atmosphere will be zero in the long term, while fossil fuels gives a net increase. Life cycle analyses (LCA) of bioethanol as a fuel have shown that emissions of CO<sub>2</sub> and other greenhouse gases are lower than when just using gasoline as a fuel in transport systems (Niven, 2005). Especially ethanol produced from lignocellulosic feedstock is reducing the emissions of fossil CO<sub>2</sub> by up to 90%.



9.7 Flow chart of different steps in bioethanol pilot plant in Ö-Vik, Sweden.

Intake feedstock, (2) steaming step, (3) pre-treatment step,
reactor steps, (5) membrane filter press to remove lignin,
detoxification step, (7) fermentation step, (8) yeast separator stage, (9) distillation system, (10) evaporation step, and (11) storage tank (with permission from Swedish Energy Agency and SEKAB for

# 9.7 Future trends

reproduction).

Developing feasible cellulosic ethanol production requires a solution of several challenges, i.e. collection and handling of feedstock in an effective way. The cost of collection and production of feedstock from forest and farmland must be reduced. New methods for increasing the bulk density of the raw material such as pelletising or briquetting must be applied to reduce the transport cost.

Another challenge is related to production costs and an effective and optimised bioethanol production process. Several steps in the process have to be further developed to increase the yield of bioethanol and to reduce the production time. It is also important to develop efficient processes for a number of different feedstocks, since there is not one single process that is suitable and optimised for all biomass. It is important to identify all factors such as material composition that may have effect on profitability of the bioethanol production facilities and optimise their lifetime.

Integration of bioethanol production with other production is important. Preparation of additional products from bioethanol by simple reactions like production of acetic acid, ethyl acetate, etc. will increase the profitability of bioethanol production. It is also essential to recover the solid rest from bioethanol process like lignin and use it as feedstock for other industrial production, e.g. fine chemicals production. Most of the lignin can be used as fuel in energy production in the bioethanol production facilities as well.

The size of bioethanol production plants must be optimised for available feedstock and to be able to produce bioethanol by high capacity all the time to reduce cost of bioethanol production. Environmental impacts of feedstock production such as effect on soil quality, biodiversity and habitat must be considered. Government support of bioethanol production in form of reduced taxes during some years can be helpful for establishment of industrial bioethanol production.

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**Abstract:** This chapter provides an overview on biological butanol production, starting with its historical importance and ending with its current and future development. Detailed descriptions of the anaerobic bacteria employed for fermentation and their respective enzymatic reactions involved are provided. The contribution also focuses on molecular biology, i.e. organization of genes and operons required for butanol formation, their transcriptional regulation, and strain improvement by metabolic engineering. Of special importance are current and possible future feedstocks, bioreactor and process technology, and downstream processing. Modelling of the process, limitations by solvent toxicity and bacteriophage infections as well as future trends of the biotechnological application are discussed.

**Key words:** butanol, *Clostridium acetobutylicum*, *Clostridium beijerinckii*, fermentation, solventogenesis.

# 10.1 Introduction

Exploding crude oil prices in the summer of 2008 once again demonstrated the dependence of world's transportation needs on fossil fuel. The situation is getting even more dramatic: experts expect worldwide energy consumption to grow by approximately 60% within the upcoming two decades (Energy Information Administration, 2007). However, fuels from fossil sources will not be able to meet this demand as they are a finite reserve. Another problem associated with burning fossil fuels is the phenomenon of global warming. The generated  $CO_2$  contributes tremendously to the so-called greenhouse effect.

Thus, the need for alternative fuels (both independent of fossil resources and  $CO_2$ -neutral) is evident. Biofuels, derived from sustainable biomass, are the most promising alternative energy source for the transportation sector. Today, only bioethanol and biodiesel are available in large quantities. However, there are also a number of disadvantages associated with them. Ethanol is hygroscopic and thus might lead to corrosion at higher blends or longer storage of blends. Not all car engines are suited for use of ethanol blends. Even 10% ethanol cannot be used in a number of models. Similarly, impurities in biodiesel prevent their usage in an ever increasing number of modern diesel engines. A solution to the problem might be the use of butanol, which can be obtained biotechnologically and has superior properties compared to ethanol and biodiesel. Butanol can be used in pure form or at any blend ratio, without causing damage to car engines. A derivative (dibutyl ether) has the potential for a diesel fuel. Finally, recent developments prove that this alcohol can be biologically produced from substrates not used for nutrition,

thus avoiding the food versus fuel problem and rendering butanol as an extremely promising candidate for a second-generation biofuel.

# 10.2 Principles, materials and feedstocks

## 10.2.1 Organisms

Microbial butanol synthesis was first noticed by famous French scientist Louis Pasteur in 1862 (Pasteur, 1862). While his organism *Vibrion butyrique* presumably represented a mixed culture, a pure culture was isolated a few years later by Albert Fitz (Fitz 1876, 1877, 1878, 1882). Around the turn of the twentieth century, further butanol-producing bacteria were isolated by many other scientists, amongst them are Martinus Beijerinck and Sergei Winogradsky. Probably, all of these isolates were members of the genus *Clostridium*, a term that was only used as a morphological description (from Greek kloster = small spindle) at that time. However, most of these strains were lost over the years (Dürre, 2001; Dürre, 2005a; Dürre and Bahl, 1996).

In 1913, Charles Weizmann isolated a strain, which produced significantly higher butanol yields (Weizmann, 1915) and later became known as *Clostridium acetobutylicum* (McCoy *et al.*, 1926). In succession, many similar strains were isolated and also designated as *C. acetobutylicum*. Only at the beginning of the 1990s, it was discovered that actually four different species (*C. acetobutylicum, Clostridium beijerinckii, Clostridium saccharobutylicum* and *Clostridium saccharoperbutylacetonicum*) were industrially used (Jones and Keis, 1995; Keis *et al.*, 2001).

Other *Clostridium* species (see Table 10.1 and Fig. 10.1) are able to form minor amounts of butanol as well (Dürre, 2005a; Dürre and Bahl, 1996). However, aside from this genus, only *Thermoanaerobacterium thermosaccharolyticum* (formerly *Clostridium thermosaccharolyticum*; Collins *et al.*, 1994), *Butyribacterium methylotrophicum* and the archeon *Hyperthermus butylicus* are known to produce 1-butanol (see Table 10.1 and Fig. 10.1). While the respective mechanisms in these organisms are still unclear (Brügger *et al.*, 2007; Grethlein *et al.*, 1991), butanol formation in clostridia has already been investigated extensively.

# 10.2.2 Principles

Model organism for the solventogenic clostridia is *C. acetobutylicum*. The metabolism of this organism is well understood, and the genes and enzymes needed for butanol production are already identified and characterized (see below and Fig. 10.2). *C. acetobutylicum* typically performs a biphasic fermentation, often referred to as ABE (for acetone/butanol/ethanol) fermentation (Dürre, 2005a; Jones and Woods, 1986).

During exponential growth (in the so-called acidogenic phase or acidogenesis), *C. acetobutylicum* follows the standard butyric acid pathway producing acetate, butyrate,  $CO_2$  and  $H_2$  (see Fig. 10.2). In addition, small amounts of ethanol and

Genus	Species	Reference		
Butyribacterium	methylotrophicum	Grethlein <i>et al.</i> , 1991		
Clostridium	acetobutylicum	Keis <i>et al.,</i> 2001		
		McCoy <i>et al.</i> , 1926		
	aurantibutyricum	George <i>et al.</i> , 1983		
	beijerinckii	Keis <i>et al.</i> , 2001		
		George <i>et al.</i> , 1983		
	butyricum	Zoutberg et al., 1989		
	cadaveris	George et al., 1983		
	carboxidivorans	Liou <i>et al.</i> , 2005		
	chauvoei	Cortiñas <i>et al.</i> , 1994;		
		Brooks <i>et al.</i> , 1976		
	felsineum	McClung and McCoy, 1935		
	pasteurianum	Harris <i>et al.</i> , 1986;		
		George <i>et al.</i> , 1983		
	puniceum	Holt <i>et al.</i> , 1988		
	roseum	McCoy and McClung, 1935		
	saccharobutylicum	Keis <i>et al.</i> , 2001		
	saccharoperbutylacetonicum	Keis <i>et al.</i> , 2001		
	septicum	Brooks <i>et al.</i> , 1976		
	sporogenes	George <i>et al.</i> , 1983		
	tetanomorphum	Gottwald et al., 1984		
Hyperthermus	butylicus	Zillig <i>et al.</i> , 1990		
Thermoanaerobacterium	thermosaccharoyticum	Freier-Schröder et al., 1989		

Table 10.1 Butanol-producing microorganisms



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*10.1* Relationship of butanol-producing microorganisms. Tree was created with Ribosomal Database Project (Cole *et al.*, 2007) on the basis of 16s rRNA gene sequences.



*10.2* Catabolic pathways of acid and solvent formation in *Clostridium acetobutylicum*. The single reactions shown do not represent stoichiometric fermentation balances.

acetoin are formed successively, and under certain conditions, lactate is produced as well. Typically, about twice as much butyrate is formed compared to acetate. Accumulation of the excreted acids causes a rapid decrease in pH of the surrounding medium. This poses a serious threat to *C. acetobutylicum*, since anaerobic bacteria are unable to maintain a constant internal pH, which is generally 1 unit higher than the external pH (Dürre *et al.*, 1988; Gottwald and Gottschalk, 1985; Huang *et al.*, 1985). When the external pH drops to the critical point of 4.5, considerable levels of undissociated acetic and butyric acid are present ( $pK_a$  of acetic acid = 4.75 and  $pK_a$  of butyric acid = 4.82), which can then pass the cytoplasmatic membrane via diffusion. Due to the higher internal pH, these acids dissociate into salts and protons again and thus destroy the essential proton gradient across the membrane needed for energy conservation and several transport mechanisms.

To avoid this deleterious effect, a major metabolic shift takes place in *C*. *acetobutylicum* at the end of exponential growth. The organism takes up acetate and butyrate and converts these organic acids into the solvents acetone and butanol, respectively (solventogenic phase or solventogenesis; see Fig 10.2). A butanol/acetone ratio of 2:1 is typical for *C. acetobutylicum*, whereas some strains of *C. beijerinckii* form isopropanol instead of acetone. While the reassimilation of

the excreted acids leads to an increased pH, the solvents acetone, isopropanol and, especially, butanol are also toxic for the cell (see Section 10.5). However, the cell gains enough time to initiate the formation of endospores and thus secures long-time survival.

## 10.2.3 Feedstocks

Solventogenic clostridia mainly feed on starch or sugars. It is strain dependent which of these substrates is preferred. While the original Weizmann strain was best suited for growth on starch, later isolations focused on sugar as a substrate. Usually, corn (starch) or molasses from sugar beet and sugar cane (sugar) are used for industrial fermentations (Ezeji *et al.*, 2005). In addition, many other substrates (Table 10.2) have been used with varying success (Dürre, 1998; Ezeji *et al.*, 2005; Jones and Woods, 1986). The use of cheese whey, for example, led to significant lower solvent productivities but considerable higher butanol/acetone ratios (up to 100:1) compared with starch and molasses (Bahl *et al.*, 1986; Maddox *et al.*, 1993).

A substrate with great potential for the future might also be lignocellulosic biomass. Solventogenic clostridia are unable to utilize lignocellulose directly, but respective hydrolysates could be used as a substrate. Industrial ABE fermentations with hydrolysates of agricultural waste have already been run in the former Soviet Union (see Section 10.3; Zverlov *et al.*, 2006), and several new processes were

Substrate	Fermentable carbon components	Reference
Algal biomass	Starch	Nakas <i>et al.</i> , 1983
Apple pomace	Fructose, glucose, sucrose	Voget <i>et al.,</i> 1985
Cassava	Starch	Chiao and Sun, 2007
Cheese whey	Lactose	Maddox <i>et al.</i> , 1993
Corn (maize, wheat, rye, millet)	Starch	Chiao and Sun, 2007; Ezeji <i>et al.</i> , 2005; Killeffer, 1927; Weizmann, 1915
Jerusalem artichokes	Fructan	Marchal <i>et al.</i> , 1985
Molasses (sugar cane, sugar beet)	Fructose, glucose, sucrose	Ezeji <i>et al.</i> , 2005; Jones, 2001
Potatoes	Starch	Gutierrez <i>et al.</i> , 1998; Grobben <i>et al.</i> , 1993; Weizmann, 1915; Fernbach and Strange, 1911a, 1911b, 1912
Sweet potatoes	Starch	Chiao and Sun, 2007; Ezeji <i>et al.</i> , 2005

Table 10.2 Substrates for ABE fermentation

tested in the last few years (Ezeji *et al.*, 2007). However, to be economically suitable, all these processes are (still) too expensive and ineffective.

#### 10.2.4 Genes, enzymes, regulation

*C. acetobutylicum* was the first completely sequenced *Clostridium*. The genome sequence of the type-strain ATCC 824 (Weyer and Rettger, 1927) was already released in 2001 by Nölling *et al.* This provided valuable information and helped in further understanding of solventogenic clostridia. Meanwhile, the genome sequence of another major solventogenic *Clostridium* species, *C. beijerinckii* NCIMB 8052, is available too (JGI, 2005). While the genome of *C. acetobutylicum* consists of a 3.94-Mbp chromosome and a 192-kbp megaplasmid pSOL1, *C. beijerinckii* contains no megaplasmid but has a significantly larger chromosome with a size of 6.0 Mbp.

One surprising finding in the genome sequence of *C. acetobutylicum* was the presence of 11 genes, whose products were unambiguously identified as cellulosome components (Nölling *et al.*, 2001; Sabathé, Bélaich, *et al.*, 2002). Although overexpression of single genes led to functional proteins (Lopéz-Contreras *et al.*, 2003; Perret *et al.*, 2004) and also a minicellulosome could be produced *in vivo* (Sabathé and Soucaille, 2003), *C. acetobutylicum* is unable to ferment cellulose (Lee *et al.*, 1985a; Lopéz-Contreras *et al.*, 2003).

However, xylan, another major component of lignocellulose besides cellulose, can be degraded by *C. acetobutylicum* as well as *C. beijerinckii* (Lemmel *et al.*, 1986; Qureshi *et al.*, 2006), and respective enzymes have been isolated and characterized (Ali *et al.*, 2004; Ali *et al.*, 2005; Lee and Forsberg, 1987; Lee *et al.*, 1985b; Lee *et al.*, 1987).

Several  $\alpha$ -amylases for degradation of starch were found in *C. acetobutylicum*. Two of them were purified and analyzed in detail (Annous and Blaschek, 1994; Paquet *et al.*, 1991), but only one of the respective genes (*amyP* = CAP0168) has been confidently identified from the genome sequence (Sabathé, Croux, *et al.*, 2002).

Mono- and disaccharides are then taken up by phosphoenolpyruvate-dependent phosphotransferase systems, which are already well described in *C. acetobutylicum* and *C. beijerinckii* (see Table 10.3). Only galactose is transported by a non-phosphotransferase mechanism (Mitchell and Tangney, 2005).

Inside the cell, sugars are metabolized to pyruvate, hexoses via glycolysis and pentoses via the pentose phosphate pathway. Respective genes were found in the genome sequence of *C. acetobutylicum* (Nölling *et al.*, 2001) and *C. beijerinckii* (JGI, 2005). Pyruvate is then converted to acetyl-CoA by a pyruvate:ferredoxin-oxidoreductase, one of the most oxygen-sensitive enzymes known (Meinecke *et al.*, 1989). Lactate and acetoin are also produced from pyruvate (Fig. 10.2), catalyzed by lactate dehydrogenase (Freier and Gottschalk, 1987) and acetolactate synthase plus acetolactate decarboxylase, respectively, while the formation of acetate, butyrate, ethanol, acetone, isopropanol and butanol starts from acetyl-CoA (Fig. 10.2).

PTS substrate	C. acetobutylicum	C. beijerinckii
Cellobiose	Mitchell and Tangney, 2005	_
Fructose	Mitchell and Tangney, 2005	Mitchell, 1996
Glucose	Tangney and Mitchell, 2007	Mitchell et al., 1991
Lactose	Yu <i>et al.</i> , 2007	Mitchell and Tangney, 2005
Maltose	Tangney <i>et al.</i> , 2001	
Mannitol	Behrens et al., 2001	Mitchell, 1996
Sorbitol		Tangney, Brehm, <i>et al.</i> , 1998
Sucrose	Tangney and Mitchell, 2000	Tangney, Rousse, et al., 1998

Table 10.3	Phosphotransferas	e systems in	C. acetobutylicum	and C.	beijerinckii
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Acetate is produced via acetyl phosphate by successive action of phosphotransacetylase (Pta) and acetate kinase (Ack) (Fig. 10.2). The latter was purified from C. acetobutylicum and was shown to be a highly specific enzyme (Winzer et al., 1997). The respective genes pta and ack are located in a common operon (CAC1742-CAC1743; Fig. 10.3) on the genome of C. acetobutylicum (Boynton et al., 1996) and are also present in C. beijerinckii, arranged in exactly the same order. Butyrate is formed in analogous reactions from butyryl-CoA (Fig. 10.2). The respective enzymes phosphotransbutyrylase (Ptb) and butyrate kinase (Buk) are already characterized in detail (Hartmanis, 1987; Thompson and Chen, 1990; Wiesenborn *et al.*, 1989b). The corresponding genes *ptb* and *buk* are clustered in a common operon on the genome of C. acetobutylicum (CAC3075-CAC3076; Fig. 10.3; Cary et al., 1988; Walter et al., 1993) and C. beijerinckii, respectively. Gene expression is relatively stable over the whole growth, similar to *pta* and ack (Fig. 10.3; Alsaker and Papoutsakis, 2005). However, in contrast to the acetate-producing enzymes, butyrate kinase activity can also be detected during solventogenesis (Andersch et al., 1983; Hartmanis and Gatenbeck, 1984). This might be attributed to a second butyrate kinase (BKII) found in C. acetobutylicum, whose physiological function is yet unknown (Huang et al., 2000).

Butyryl-CoA itself is produced from two molecules of acetyl-CoA by successive action of thiolase (ThIA), 3-hydroxybutyryl-CoA dehydrogenase (Hbd), crotonase (Crt) and butyryl-CoA dehydrogenase (Bcd) (Fig. 10.2). The respective genes are clustered on the genome of *C. acetobutylicum* and *C. beijerinckii* in the *bcs* operon (CAC2708-CAC2712; Fig. 10.3; Boynton *et al.*, 1996), except the thiolase gene *thlA* (CAC2873) that is organized monocistronically (Stim-Herndon *et al.*, 1995). Furthermore, a second thiolase operon was found on the megaplasmid of *C. acetobutylicum* (Winzer *et al.*, 2000). While its physiological role is still unknown, ThIA has already been studied in detail (Wiesenborn *et al.*, 1988). Hbd has been purified and characterized from *C. beijerinckii* (Colby and Chen, 1992) and Crt from a non-specified *C. acetobutylicum* strain (Waterson *et al.*, 1972). Data on Bcd are scarce, but Inui *et al.* (2008) demonstrated that a pair of electron-transferring flavoproteins (EtfA/B), whose genes are also part of the *bcs* operon,



*10.3* Arrangement of the genes associated with solvent formation in *C. acetobutylicum* and their expression profile (according to Alsaker *et al.*, 2004).

is essential for the activity of this enzyme. In *Clostridium kluyveri*, Bcd was shown to form a stable complex with EtfA/B (Herrmann *et al.*, 2008; Seedorf *et al.*, 2008), which is also involved in energy conservation via an Rnf complex (Herrmann *et al.*, 2008; Seedorf *et al.*, 2008). However, no Rnf complex is present in *C. acetobutylicum*, while respective genes were found in *C. beijerinckii*.

Formation of solvents starts with an acetoacetyl-CoA:acetate/butyrate-CoA transferase CtfA/B, which converts the previously produced acids acetate and butyrate into the respective acyl-CoA derivatives and acetoacetate (Fig. 10.2). While the recycled acetyl-CoA and butyryl-CoA are used for the production of alcohols such as ethanol and butanol via a number of aldehyde and alcohol dehydrogenases (see below), an acetoacetate decarboxylase Adc splits acetoacetate into  $CO_2$  and acetone, which is in some strains of *C. beijerinckii* further reduced to isopropanol by action of a primary/secondary alcohol dehydrogenase (Ismaiel *et al.*, 1993).

CoA transferase and acetoacetate decarboxylase have already been studied in detail (Chen, 1993; Gerischer and Dürre, 1990; Petersen and Bennett, 1990; Schaffer et al., 2002; Wiesenborn et al., 1989a). In C. acetobutylicum, the respective genes are located on the megaplasmid directly next to each other in a convergent direction (Fig. 10.3). While adc forms a monocistronic operon, ctfA/B are arranged in the sol operon together with the genes orfL (encoding a small peptide of still unknown function) and *adhE* (coding for a bifunctional butyraldehyde/butanol dehydrogenase) (Fischer et al., 1993; Zickner et al., 1993). This distinguishes C. acetobutylicum from all other solventogenic clostridia, where *adc* is part of the *sol* operon and *adhE* is replaced by an *ald* gene encoding an aldehyde dehydrogenase (Berezina et al., 2009; Toth et al., 1999). A typical  $\sigma^{A}$ -dependent promoter was found upstream of *adc* (Gerischer and Dürre, 1992), whereas two promoter sequences were deduced for the sol operon by primer extension experiments (Fischer et al., 1993; Nair et al., 1994b). However, reporter gene studies revealed that only the distal sequence P<sub>1</sub> represents a promoter and the proximal P<sub>2</sub> is obviously an mRNA processing site (see below; Thormann et al., 2002). Both operons show a similar expression profile with a massive upregulation at transition from acidogenesis to solventogenesis (Fig. 10.3; Alsaker and Papoutsakis, 2005). The signal leading to this induction is still unknown, but it is proposed that various extra- and intracellular parameters such as temperature, low pH and high concentration of (undissociated) acetic and butyric acid (Ballongue et al., 1985; Gottwald and Gottschalk, 1985; Huesemann and Papoutsakis, 1986; Monot et al., 1983; Terracciano and Kashket, 1986), limiting phosphate or sulphate concentrations (Bahl, Andersch, and Gottschalk, 1982; Kanchanatawee and Maddox, 1990), levels of butyryl phosphate and butyryl-CoA (Boynton et al., 1994; Gottwald and Gottschalk, 1985; Zhao et al., 2005), ATP/ ADP ratio and NAD(P)H level (Grupe and Gottschalk, 1992) are involved. All these factors result in less negative supercoiling and thus relaxation of DNA. This change in topology could serve as a transcriptional sensor by allowing or restricting regulatory proteins to bind (Wang and Syvanen, 1992; Wong and Bennett, 1996; Ullmann and Dürre, 1998; Ullmann et al., 1996). Several binding motifs have been identified in intergenic regions of sol and adc; three binding sites for the master regulator of sporulation SpoOA were found upstream of the adc promoter and another 0A box is located upstream of the sol promoter (Ravagnani et al., 2000). Gel retardation and targeted mutation experiments confirmed binding of phosphorylated Spo0A to these sites (Hollergschwandner, 2003; Ravagnani et al., 2000), thus proving that the regulatory networks of solventogenesis and sporulation are linked. Furthermore, a potential binding site for the catabolite control protein CcpA (cre sequence; Feustel, 2004; Nold, 2008) and three imperfect repeats (R1, R2 and R3; Thormann et al., 2002; Scotcher et al., 2003) were found upstream of the sol promoter. The region downstream of the sol promoter forms a very complex secondary structure with several predicted stem loops. This structure seems to be important for processing of the adhE mRNA (Thormann *et al.*, 2002), but might also affect the *adhE* expression negatively (Scotcher *et al.*, 2003).

The *adhE* transcript finally yields two different products, the mature bifunctional enzyme and the C-terminal alcohol dehydrogenase, probably due to a second translation start within the same mRNA (Thormann et al., 2002). While overproduction of AdhE in C. acetobutylicum leads to increased NAD+-dependent butyraldehyde/acetaldehyde dehydrogenase activity and NADH-dependent butanol/ethanol dehydrogenase activity (Nair et al., 1994a), only minor aldehyde dehydrogenase activity could be detected after purification (Thormann, 2001). Heterologous overexpression in Escherichia coli resulted in no enzyme activity at all (Lorenz, 1997; Nair et al., 1994a). In addition to AdhE, two butanol dehydrogenases BdhA and BdhB (sometimes also referred to as BdhI and BdhII) are present in C. acetobutylicum. Although these isoenzymes have a high identity, BdhB has a significantly better affinity to butyraldehyde than BdhA (Petersen et al., 1991; Walter et al., 1992). The respective genes are organized in monocistronic operons directly next to each other on the genome of C. acetobutylicum (Fig. 10.3). In C. beijerinckii, three different butanol dehydrogenases could be identified (Chen, 1995) in addition to the aldehyde dehydrogenase Ald (Toth et al., 1999; Yan and Chen, 1990).

Under special conditions of high NAD(P)H availability, a second bifunctional alcohol/aldehyde dehdrogenase AdhE2 is formed in *C. acetobutylicum*, representing the first case of an organism that possesses two such enzymes (Fontaine *et al.*, 2002). Such conditions could be induced by addition of artificial electron carriers such as methyl viologen dyes (Rao and Mutharasan, 1986, 1987) or growth on reduced substrates such as glycerol (Fontaine *et al.*, 2002) and lead to alcohologenic fermentations with butanol and increased levels of ethanol, but no acetone as products (Girbal *et al.*, 1995). The gene *adhE2* is also located on the megaplasmid of *C. acetobutylicum* and organized as a monocistronic operon approximately 47 kbps upstream of the *sol* operon. A homologous gene is present in the genome of *C. beijerinckii* as well.

# 10.3 Process technologies and techniques

## 10.3.1 ABE fermentation history

Industrial ABE fermentation started almost 100 years ago in 1913. At that time, the rapidly growing automobile industry required high amounts of rubber for tires. Since butanol could be used as a precursor of butadiene (the starting material for the synthetic rubber production), the British company Strange and Graham, Ltd. launched a project to investigate microbial butanol formation. They employed William Perkins and Charles Weizmann from Manchester University and Auguste Fernbach and Moïse Schoen from Institute Pasteur in Paris. Soon after, Fernbach isolated a respective strain and Strange and Graham, Ltd. started ABE fermentation

at a plant in Rainham, UK, and later on in King's Lynn, UK (Fernbach and Strange, 1911a, 1911b, 1912).

However, due to increased production from Asian plantations, rubber prices dropped again, but the outbreak of World War I led to a sudden demand for acetone (as a solvent for the production of the smokeless propellant cordite). Therefore, the British government contracted Strange and Graham, Ltd., which produced an average of 970 pounds acetone per week (Gabriel, 1928). Weizmann, who meanwhile had left the group, succeeded with the isolation of C. acetobutylicum (see Section 10.2). Originally, he had planned to publish his results as scientific contribution, but when he realized that his discoveries might be helpful to the empire, he changed his mind and applied for a patent (Weizmann, 1915). Since Weizmann's results were so promising, the British government decided to adapt six distilleries for the Weizmann process and also requested Strange and Graham, Ltd. to switch to the Weizmann process. Consequently, their production increased to over 2200 pounds acetone per week (Gabriel, 1928). However, due to the German submarine offensive in the Atlantic, maize and grain, which were needed as feedstock for the Weizmann process, could not be imported in required quantities anymore. Therefore, horse chestnuts collected by school children were used as alternative feedstock (Hastings, 1978; Imperial War Museum Collections, 2009), and the British government decided to build new plants in Canada and India, where sufficient raw materials were available. While the plant in India was never completed, a plant in Toronto began operation in 1916 and another plant was constructed in Terre Haute, Indiana, after the United States entered the war (Gabriel, 1928). This secured the constant supply of acetone and was a decisive factor for the allied victory. To express their gratefulness, the British government wanted to honor Weizmann. However, he rejected any acknowledgments, but as a Zionist addressed the issue of a Jewish homeland in Palestine. When the state of Israel was finally founded in 1948, Weizmann became its first president.

After peace was established, no more acetone was needed and all plants were shut down. However, some effort was made to salvage the 'useless' butanol that had accumulated during the war and had simply been stored in large tanks. While some butanol was converted to methyl ethyl ketone (MEK), it was found that butanol and its ester butyl acetate can also be used directly as a replacement of fusel oil and amyl acetate, respectively (Gabriel, 1928; Killeffer, 1927). The latter was needed in large quantities by the booming automobile industry (as solvent for lacquers) and had so far been produced from amyl alcohol. However, since amyl alcohol is obtained as a side product of the ethanol fermentation, it became unavailable when the prohibition was introduced in the United States in 1919. Butanol fermentation became lucrative again, and the newly founded Commercial Solvents Corporation of Maryland (CSC) acquired the rights to the Weizmann process as well as the Terre Haute plant from the Allied War Board in the very same year. However, the general business slump of 1920 forced a nine-month shutdown and a bacteriophage infection (see Section 10.5) in 1923 cut yields in

half for almost a year (Gabriel, 1928; Jones *et al.*, 1986). Nevertheless, the capacity of the Terre Haute plant was increased from 40 to 52 fermenters and a new plant was built in Peoria, Illinois, consisting of thirty-two 50000-gallon fermenters and eventually enlarged to 96 fermenters (Gabriel, 1928). Strange and Graham also tried to get back into business but went into liquidation after a lost lawsuit against CSC (Ross, 1961). When the Weizmann patent finally expired in 1936, new plants were opened in Philadelphia, Pennsylvania, and Baltimore, Maryland, the UK, the former Soviet Union, Brazil, Australia, South Africa, Puerto Rico, Egypt, Japan, and the former Japanese colony Formosa (today's Taiwan) (Jones and Woods, 1986; McCutchan and Hickey, 1954). At that time, butanol was predominately produced biologically by ABE fermentation (Dürre, 2005a). During World War II, the focus shifted to acetone production again, and semi-continuous fermentations and continuous distillation methods were successfully used for the first time (Hastings, 1971, 1978).

However, a few years after the end of the war, the petrochemical industry overcame the ABE fermentation due to rising substrate prices (Dürre, 2005a). Thus, the process was only continued in politically isolated countries. In apartheid South Africa, the National Chemical Products (NCP) company was operating an ABE fermentation plant in Germiston with twelve 90 000-1 fermenters until 1983 (Jones, 2001; Jones and Woods, 1986). Their process relied on batch fermentations with molasses as substrate and showed remarkable efficiency and reliability. Each run had a length of around 30 hours and yielded a solvent concentration of 17-19 g/l (with an acetone ratio of 32-36%) from 5.5-7% sugar (Jones, 2001; Jones and Woods, 1986). Later on, it was shown that the NCP production strains belonged to two species, C, beijerinckii and C, saccharobutylicum (Jones, 2001; Keis et al., 2001). In the former Soviet Union, ABE fermentation was also carried out until the late 1980s in at least eight plants (the biggest in Dokshukino). The initial process was similar to the one from Weizmann, utilizing C. acetobutylicum in starch-based batch fermentations (Jones, 2001; Zverlov et al., 2006). However, over the years, the process was developed to continuous mode with molasses and wheat or rye flour, but also agricultural waste hydrolysates as substrate. An average fermentation run yielded 10 g/l of butanol, 6.4 g/l of acetone and 1.5 g/l of ethanol from 4.7% sugar equivalents (mixtures of starch, maltodextrines, sucrose and pentoses). For the Evremovo plant, a yearly production of 15000-ton solvents (8550 tons butanol, 4140 tons acetone and 2310 tons ethanol) was calculated (Zverlov et al., 2006). While most other countries shut down their ABE fermentation plants, the People's Republic of China opened its first plant in 1950 at Shanghai (Chiao and Sun, 2007). In the following years, the Chinese ABE fermentation industry expanded rapidly. At its peak during the 1980s, more than 30 plants were operating, producing around 170000 tons of solvents per year. Most plants were using starchy materials such as corn, cassava, potato or sweet potato as feedstock, whereas some plants also relied on molasses as substrate, utilizing different isolates of C. acetobutylicum. The process started as batch
fermentation but was later developed into a continuous process up to ca. 200 hours (Chiao and Sun, 2007). However, during the 1990s, the number of ABE fermentation plants decreased, and in 2004, the last plant was closed.

Only three years later, China resumed production at 11 plants with a total capacity of 410 000-ton solvents per year, which is expected to be extended to over 1 000 000 tons soon (Ni and Sun, 2009). Recently, a new plant was opened in Brazil too (Jones, 2008). Furthermore, several companies such as Butalco, Butamax<sup>TM</sup> (a joint venture of BP and DuPont), ButylFuel, Cathay Industrial Biotech, Cobalt Biofuels, Gevo, Green Biologics, METabolic EXplorer or Tetravitae Bioscience compete to commercialize ABE fermentation on a global basis again. While Cathay Industrial Biotech is already running a 30 000-ton solvents per year plant in Jilin, China (Ni and Sun, 2009), Gevo operates a one million gallon butanol per year demonstration plant in St. Joseph, Missouri (Gevo, 2009) and Butamax<sup>TM</sup> is constructing a pilot plant at Wissington, UK, to produce an annual 30 000-ton butanol from 2010 onwards (BP and DuPont, 2006; Butamax<sup>TM</sup>, 2009).

#### 10.3.2 Fermentation processes (batch/continuous)

The ABE fermentation of sugars and starch meanwhile is a mature process. The simplest method is batch fermentation combined with distillation (see below) to separate the solvents from the culture. Depending on the choice of substrate, it takes from around 30 hours up to six days to complete a run. Using this method, cell concentrations of up to 4 g/l and maximal solvent concentrations of 16–20 g/l (with a productivity of up to 0.5 g/l/h) could be reached, before solvent toxicity (see Section 10.5) inhibits further growth.

Higher yields could be achieved in fed-batch or continuous fermentations, but it is essential to have a proper product removal process in place (see below; Eckert and Schügerl, 1987; Ezeji et al., 2004). However, during prolonged or continuous cultivation, cells show a tendency to lose the ability to produce solvents. In C. acetobutylicum, this effect could be traced back to loss of the megaplasmid pSOL1 (Bahl, Andersch, and Gottschalk, 1982; Cornillot et al., 1997), which contains most of the genes required for solvent production (see Section 10.3). However, strain degeneration can also occur in C. beijerinckii (Kashket and Cao, 1993), which does not harbor any plasmids at all. Two systems were developed to monitor strain degeneration, using infrared spectrometry (Schuster et al., 2001) or real-time PCR (Lee et al., 2010) methods, respectively. However, it is possible to prevent strain degeneration in C. acetobutylicum cultures by limiting phosphate (Ezeji et al., 2005) and in C. beijerinckii cultures by addition of 20 mM sodium acetate (Chen and Blaschek, 1999a, 1999b). Another problem is the biphasic nature of the clostridial metabolism (see Section 10.2), which is not well suited for continuous fermentations. To overcome this issue, butyrate feeding was applied (Bahl, Andersch, Braun, et al. 1982; Qureshi et al., 2004; Tashiro et al., 2004) and two-stage (Bahl, Andersch, and Gottschalk, 1982; Godin and Engasser, 1990; Mutschlechner *et al.*, 2000) or multi-stage (Ni and Sun, 2009; Zverlov *et al.*, 2006) fermentations were designed.

The use of immobilized bioreactors proved to be advantageous as well, not only to increase the length of fermentation but also to increase cell concentrations and reaction rates (Qureshi, Annous, *et al.*, 2005). Immobilized cell techniques have already been applied for ABE fermentation since the 1980s (Krouwel *et al.*, 1983), and various supports and reactor configurations (Table 10.4) have meanwhile been tested with great success. In a plug-flow reactor using clay brick as a support, a reactor productivity of 16.2 g/l/h could be achieved with *C. beijerinckii* (Lienhardt *et al.*, 2002), while cell concentrations of 74 g/l were reported for *C. acetobutylicum* in a packed bed reactor with bone charcoal as support (Qureshi *et al.*, 1988). Another possibility to achieve high cell concentrations is the use of cell recycle reactors (Yang and Tsao, 1995). However, fouling of membranes is often a problem with such processes.

Regardless of the fermentation method, attention should be paid to some general factors. It is important to maintain a redox potential of -250 mV or less (Kim *et al.*, 1988), since the pyruvate:ferredoxin-oxidoreductase (one of the key enzymes of the clostridial metabolism; see Section 10.2) transfers electrons at a very low potential (Meinecke *et al.*, 1989). Another critical point is the pH value (see Section 10.2). Although low amounts of butanol can be produced at a neutral pH (Fontaine *et al.*, 2002; Holt *et al.*, 1984), in general, a low pH value is required for solvent production. However, if the pH decreases too fast (e.g. in poorly buffered media), a sudden termination of solventogenesis (known as 'acid crash') may occur (Maddox *et al.*, 2000).

Support	Organism	Reactor type	Reference
Alginate	C. beijerinckii C. saccharobutylicum	CTSR FBR	Krouwel <i>et al.,</i> 1983 Largier <i>et al.,</i> 1985
Beechwood shavings	C. acetobutylicum	CTSR	Förberg and Häggström, 1985
Bone charcoal	C. acetobutylicum	PBR	Qureshi <i>et al.</i> , 1988; Friedl <i>et al.</i> , 1991
		FBR	Qureshi and Maddox, 1989
Clay brick	C. beijerinckii	PFR	Qureshi <i>et al.</i> , 2000; Lienhardt <i>et al.</i> , 2002
Coke	C. acetobutylicum	CTSR	Welsh <i>et al.</i> , 1987
Corn stalk	C. beijerinckii		Zhang <i>et al.</i> , 2009
Glass beads	C. acetobutylicum	PBR	Qureshi, Annous, et al., 2005
Natural sponge	C. acetobutylicum	TBR	Park <i>et al.</i> , 1989
Polyester sponge	C. acetobutylicum	TBR	Park <i>et al.</i> , 1990

Table 10.4 Immobilized bioreactors for ABE fermentation

Note: CTSR = continuous stirred tank reactor, FBR = fluidized-bed reactor, PBR = packed-bed reactor, PFR = plug-flow reactor, TBR = trickle-bed reactor.

#### 10.3.3 Downstream processing

The traditional product recovery process is distillation carried out at the end of growth. The separation is a result of the different boiling points of water (100°C at standard pressure), acetone (56°C), butanol (117°C) and ethanol (78°C). High energy and disposal costs notwithstanding this technique is still used for batch fermentations. However, continuous fermentations require integrated recovery techniques, since high butanol concentrations in the fermentation broth are growth limiting (see Section 10.5).

Adsorption is an attractive alternative, which can be used *in situ* and has a low energy requirement (Qureshi, Hughes, *et al.*, 2005). On the other hand, this technique offers only a low selectivity and nutrients are often removed from the media as well. Moreover, the prices of the resins are (still) too high.

A relatively inexpensive and simple method is gas stripping (Ennis *et al.*, 1986; Ezeji *et al.*, 2004; Groot *et al.*, 1989). During the ABE fermentation, high amounts of  $CO_2$  and  $H_2$  gases are generated, which could be used to capture the solvents from the fermentation broth. The gases are sparged through the fermentation broth, cooled down in a condenser to strip off the solvents, and then recycled back into the fermenter to recover more solvents. However, this technique is not capable of a complete solvent removal from the fermentation broth and also has a low selectivity.

A method that offers higher selectivity is liquid–liquid extraction, in which a water insoluble organic extractant is mixed with the fermentation broth (Ezeji *et al.*, 2007). Since butanol is more soluble in organic than in aqueous solutions, it selectively accumulates in the organic phase of the extractant. However, only few non-toxic extractants such as oleyl alcohol are known.

To overcome this issue, perstraction was developed (Qureshi and Maddox, 2005), a technique by which a membrane separates the fermentation broth from the extractant. Unfortunately, membranes are generally expensive and often suffer from clogging and fouling problems.

This is also true for other recovery processes such as pervaporation (Friedl *et al.*, 1991; Geng and Park, 1994; Groot *et al.*, 1984; Izák *et al.*, 2008; Jitesh *et al.*, 2000; Larrayoz and Puigjaner, 1987; Matsumura *et al.*, 1992; Qureshi and Blaschek, 1999, 2000) and reverse osmosis (Garcia III *et al.*, 1985), which are based on selective semi-permeable membranes. Separation of the solvents is accomplished by vaporation and high pressures, respectively.

## 10.4 Modeling and optimization

#### 10.4.1 Modeling

First attempts to model the ABE fermentation were already undertaken in the 1980s (Voturba *et al.*, 1986) based on mass balances for the substrate, biomass,

key intermediates and products of C. acetobutylicum batch cultures. Better models were proposed when various on-line measurements (Chauvatcharin et al., 1998; Junne et al., 2008) and the genome sequences of C. acetobutylicum (Nölling et al., 2001) and later on C. beijerinckii (JGI, 2005) became available. Meanwhile, the study of transcriptome (Alsaker and Papoutsakis, 2005; Alsaker et al., 2004; Jones et al., 2008; Shi and Blashek, 2008; Tomas et al., 2003a, 2003b; Tomas et al., 2004; Tummala, Junne, Paredes, et al., 2003), proteome (Schwarz et al., 2007; Sullivan and Bennet, 2006) and metabolome (Shinto et al., 2007) of different solventogenic clostridia leads to more complex and comprehensive models (Junne et al., 2008; Senger and Papoutsakis, 2008a, 2008b; Shinto et al., 2007), which supported further understanding of the clostridial metabolism and allowed predictions of metabolic fluxes and end-products for several scenarios. However, the biphasic nature of the metabolism and the complex regulatory networks (see Section 10.2) still cause some problems that can result in incorrect outputs. The assumed reversibility of enzymatic activities lacks experimental evidence in several cases. Also, the obvious pH influence on the shift to solventogenesis has been neglected in some models. A transnational research network is currently focusing on elucidating systems biology of solventogenesis in C. acetobutylicum (project COSMIC within the SysMO program, www.sysmo.net).

## 10.4.2 Metabolic engineering

Since the ABE fermentation is already a mature process (see Section 10.3), the biggest potential for optimization is offered by metabolic engineering. Prerequisite is the knowledge of genome sequence and development of genetic tools, which are both available for C. acetobutylicum and C. beijerinckii. Electroporation has been established as a method of choice for gene transfer to C. acetobutylicum (Mermelstein and Papoutsakis, 1993; Nakotte et al., 1998; Tyurin et al., 2000) and C. beijerinckii (Birrer et al., 1994). For C. acetobutylicum, transformation efficiencies of up to 10<sup>5</sup>-10<sup>7</sup> transformants/ug plasmid DNA are reported (Mermelstein and Papoutsakis, 1993; Tyurin et al., 2000), but methylation of the DNA proved to be essential prior to transformation (Mermelstein and Papoutsakis, 1993). Recently, a modular system for *Clostridium* shuttle vectors was described (Heap et al., 2009), which comprises the most common origins of replication and selective markers for clostridia. During the last few years, major improvements in gene inactivation were achieved as well. Previously, it was only possible to silence genes by antisense RNA techniques (Tummala et al., 2005; Wagner and Simons, 1994) or inactivate (and respectively replace) genes by homologous recombination (Tomas et al., 2005; Tummala et al., 2005). However, the latter is very timeconsuming, since the recombination frequency of clostridia is generally not very high. Another problem is the lack of temperature-sensitive plasmids or counterselectable markers for this genus that necessitates the use of non-replicative plasmids, which are rapidly degraded inside the cell by DN ases and endonucleases. To overcome this issue, Soucaille *et al.* (2008) designed a mutant strain of *C. acetobutylicum* with an inactivated restriction endonuclease system and a deleted *upp* gene. This gene encodes an uracil phosphoribosyl-transferase, which catalyzes transformation of 5-fluorouracil into a toxic product and can now be used as a counterselective marker on a respective plasmid. An even faster method is provided by the so-called ClosTron system (Heap *et al.*, 2007; Heap *et al.*, 2010; Shao *et al.*, 2007). This system allows the rapid creation of integration mutants based on a sequence-specific group II intron from *Lactococcus lactis*.

Several genes involved in solventogenesis were already overexpressed or inactivated in *C. acetobutylicum* (Table 10.5). Highest butanol titers (238 mM) were reported for a strain with an overexpressed *adhE* and an inactivated *orf5* gene (Harris *et al.*, 2001). *orf5* is located directly upstream of the *sol* operon (Fig. 10.3) and was proposed to encode the repressor of that operon (SolR) (Nair *et al.*, 1994b). However, a more detailed study revealed that its gene product was actually localized extracellularly (which is in contrast to a transcriptional regulator) and is involved in glycosylation–deglycosylation reactions (Thormann and Dürre, 2002; Thormann *et al.*, 2002). The repressing effect observed stemmed from an intergenic region between *orf5* and the *sol* operon (Thormann *et al.*, 2002).

In addition to increasing butanol yields, some studies also focused on elimination of by-products and the improvement of substrate utilization and tolerance to a variety of stresses. Acetone formation was reduced by inactivation of acetoneproducing genes ctfA/B (Sillers et al., 2009; Soucaille, 2008; Tummala, Junne, and Papoutsakis, 2003) and adc (Jiang et al., 2009). In this context, efforts are also ongoing to engineer the C. acetobutylicum mutant strain M5, which lost the megaplasmid pSOL1 and thus does not produce acetone at all (Lee et al., 2009b; Sillers et al., 2008). The production of the acids acetate, butyrate and lactate was decreased by inactivating the phosphotransacetylase gene *pta* (Green *et al.*, 1996; Soucaille, 2008) and/or the acetate kinase gene ack (Sillers et al., 2008; Soucaille, 2008), the butyrate kinase gene buk (Green et al., 1996; Harris et al., 2000; Soucaille, 2008), and the lactate dehydrogenase gene *ldh* (Soucaille, 2008), respectively. However, the elimination of more than one by-product at the same time (in order to design a homo-butanol producer) still remains a challenging task. Especially, the elimination of ethanol as a by-product might be critical, since most butyraldehyde and butanol dehydrogenases also show activity with acetyl-CoA and acetaldehyde, respectively. To create a more robust strain, aerotolerance was prolonged by inactivation of perR (Hillmann et al., 2008) and tolerance to butanol was improved by overexpression of the groESL operon (Tomas et al., 2003b). The latter resulted in a strain that showed 85% less butanol inhibition and a prolonged metabolism that yielded 40% higher butanol titers (Table 10.5). Efforts to improve the substrate utilization of C. acetobutylicum only showed minor success so far. Xylose utilization was improved slightly by introduction of a transaldolase gene talA from E. coli (Gu et al., 2009), and overexpression of cellulosome components resulted in formation of a minicellulosome (see Section 10.2; Sabathé and Soucaille, 2003).

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Genes overexpressed	Genes inactivated	Butanol (mM)	Acetone (mM)	Ethanol (mM)	Butyrate (mM)	Acetate (mM)	Reference
adhE	orf5	238	141	47	97	87	Harris <i>et al.,</i> 2001
groESL	_	231	148	21	70	80	Tomas <i>et al.,</i> 2003
adhE	buk	226	66	98	18	113	Harris <i>et al.,</i> 2000
_	buk	225	76	57	18	111	Harris <i>et al.,</i> 2000
_	orf5	197	97	29	74	84	Harris <i>et al.,</i> 2001
_	adc	183	2	61	16	43	Jiang <i>et al.,</i> 2009
adhE	ctfB	178	61	300	1	85	Sillers <i>et al.,</i> 2009
adc, ctfA/B	_	177	149	31	0.5	10	Mermelstein <i>et al.,</i> 1993
adhE	_	160	59	76	2	124	Sillers <i>et al.,</i> 2009
adhE, ctfA/B	M5ª	154	10	20	54	227	Lee <i>et al.,</i> 2009
thIA, adhE	_	153	98	28	17	67	Sillers <i>et al.,</i> 2009
adhE	M5ª	150	_	44	87	248	Sillers <i>et al.,</i> 2008
_	buk	146	39	16	37	149	Green <i>et al.,</i> 1996
buk, ptb	_	140	80	10	30	60	Walter <i>et al.,</i> 1994
_	pta	133	72	13	159	87	Green <i>et al.,</i> 1996
adhE	ctfB	130	26	190	52	125	Tummala, Junne, and Papoutsakis, 2003
thIA, adhE	M5 <sup>a</sup>	108	—	19	84	172	Sillers <i>et al.,</i> 2008
adhE	M5ª, <i>ack</i>	92	_	22	75	180	Sillers <i>et al.,</i> 2008
adhE	M5ª	84	_	8	99	101	Nair and Papoutsakis, 1994
Wild-typ	е	131–158	79–85	11–16	71–112	76–108	Same as above
M5 <sup>a</sup>		_	_	6	169	107	Same as above

#### Table 10.5 Metabolic engineering in C. acetobutylicum

<sup>a</sup> *C. acetobutylicum* mutant strain M5, which lost the megaplasmid pSOL1 (containing genes *adhE, ctfA/B, adc, orf5* and *adhE2*) and does not produce solvents.

Meanwhile, metabolic engineering also allows butanol production in other organisms, which are easier to handle such as *E. coli, Bacillus subtilis* or the yeast *Saccharomyces cerevisiae* (Atsumi, Cann, *et al.*, 2008; Atsumi, Hanai, *et al.*, 2008; Dijk and Raamsdonk, 2009; Donaldson *et al.*, 2007; Inui *et al.*, 2008; Liao *et al.*, 2008; Nielsen *et al.*, 2009; Steen *et al.*, 2008), or have a significantly higher tolerance against butanol such as *Pseudomonas putida* (Nielsen *et al.*, 2009; Rühl *et al.*, 2009), or have the ability to grow on abundant substrates like synthesis gas such as *Clostridium ljungdahlii* (Köpke, 2009). However, the respective butanol yields are (still) insignificant compared to those of solventogenic clostridia (Table 10.6).

Organism	Modifications	Butanol (mM)	Reference
E. coli	Introduction of <i>thIA, hbd, crt, bcd,</i> <i>etfA/B</i> and <i>adhE</i> from <i>C. acetobutylicum</i> ; overexpression of <i>gapA</i>	43	Nielsen <i>et al.,</i> 2009
E. coli	Introduction of <i>thIA, hbd, crt, bcd, etfA/B</i> and <i>adhE2</i> from <i>C. acetobutylicum</i>	16.2	lnui <i>et al.,</i> 2007
Pseudomonas putida	Introduction of <i>thIA, hbd, crt, bcd, etfA/B</i> and <i>adhE</i> from <i>C. acetobutylicum,</i>	9	Nielsen <i>et al.,</i> 2009
E. coli	Introduction of <i>thIA, hbd, crt, bcd, etfA/B</i> and <i>adhE2</i> from <i>C. acetobutylicum;</i> inactivation of <i>adhE, IdhA, frdB/C, fnr</i> and <i>pta</i>	5	Atsumi, Cann, <i>et al.</i> , 2008;
			Liao <i>et al.,</i> 2008
E. coli	Introduction of <i>thIA, hbd, crt, bcd, etfA/B</i> and <i>adhE</i> from <i>C. acetobutylicum</i>	4.2	lnui <i>et al.,</i> 2007
C. ljungdahlii	Introduction of <i>thIA, hbd, crt, bcd, adhE</i> and <i>bdhA</i> from <i>C. acetobutylicum</i>	2	Köpke, 2009
Bacillus subtilis	Introduction of <i>thIA</i> , <i>hbd</i> , <i>crt</i> , <i>bcd</i> , <i>etfA/B</i> and <i>adhE2</i> from <i>C. acetobutylicum</i>	1.7	Nielsen <i>et al.,</i> 2009
Saccharomyces cerevisiae	Introduction of codon opimized <i>thIA, hbd,</i> <i>crt, bcd, etfAB, bdhB</i> and <i>adhE</i> from <i>C. acetobutylicum</i> and <i>acdh67</i> from <i>Listeria innocua</i> ; inactivation of <i>adh1</i> and <i>adh2</i>	1.26	Dijk and Raamsdonk, 2009
E. coli	Introduction of <i>thIA, hbd</i> and <i>crt</i> from <i>C. acetobutylicum, ter</i> from <i>Euglena</i> <i>gracilis</i> , and <i>ald</i> from <i>C. beijerinckii</i> ; overexpression of <i>yqhD</i>	1.03	Donaldson <i>et al.,</i> 2007
E. coli	Introduction of <i>kivD</i> from <i>Lactococcus</i> <i>lactis</i> and <i>adh2</i> from <i>Saccharomyces</i> <i>cerevisiae</i> ; overexpression of <i>ilvA</i> and <i>leuA/B/C/D</i>	0.6	Atsumi, Hanai, and Liao, 2008
			(Continued)

Table 10.6 Metabolic engineering in other organisms

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Organism	Modifications	Butanol (mM)	Reference
Bacillus subtilis	Introduction of <i>thIA</i> , <i>hbd</i> , <i>crt</i> and <i>bhdB</i> from <i>C. acetobutylicum</i> , <i>ter</i> from <i>Euglena</i> <i>gracilis</i> , and <i>ald</i> from <i>C. beijerinckii</i>	0.19	Donaldson <i>et al.</i> , 2007
Saccharomyces cerevisiae	Introduction of <i>hbd, crt</i> and <i>adhE2</i> from <i>C. beijerinckii</i> and <i>ccr</i> from <i>Streptomyces</i> <i>collinus</i> ; overexpression of <i>erg10</i>	0.03	Steen <i>et al.,</i> 2008
Saccharomyces cerevisiae	Introduction of <i>thIA, hbd, crt</i> from <i>C. acetobutylicum, ter</i> from <i>Euglena</i> <i>gracilis</i> , and <i>ald</i> from <i>C. beijerinckii</i>	0.02	Donaldson <i>et al.,</i> 2007

#### Table 10.6 Continued

Note: acdh67 = acetylating aldehyde dehydrogenase, adh1/2 = alcohol dehydrogenase, adhE/adhE2 = alcohol/aldehyde dehydrogenase, ald = butyraldehyde dehydrogenase, bcd = butyryl-CoA dehydrogenase, bdhB = butanol dehydrogenase, ccr = butyryl CoA dehydrogenase, crt = crotonase, erg10 = thiolase, etfA/B = electron transferring flavoproteins, fnr = oxygen transcriptional regulator, frdB/C = fumarate reductase, hbd = 3-hydroxybutyryl-CoA dehydrogenase, ilvA = threonine deaminase, ldhA = lactate dehydrogenase, leuA = 2-isopropylmalate synthase, leuB = 3-isopropylmalate dehydrogenase, leuC/D = isopropylmalate isomerase, n.d.a. = no data available, pta = phosphotransacetylase, ter = trans-2-enoyl-CoA reductase, th/A = thiolase, yqhD = alcohol dehydrogenase.

## 10.5 Advantages and limitations

### 10.5.1 Butanol versus ethanol

Alcoholic fuels are a perfect replacement for gasoline. Most commonly used is bioethanol with an annual production of 17335.2 million gallons in 2008 (Renewable Fuels Association, 2009). However, biobutanol offers a number of major advantages over bioethanol (Table 10.7). First and foremost, butanol has a

Fuel	Gasoline	Biobutanol	Bioethanol
Energy density (MJ/I)	32–35	21.2	29.2
Air-fuel ratio	14.6	9.0	11.2
Mileage (%)	100	61–66	83–91
Research octane number (RON)	91–99	129	96
Motor octane number (MON)	81–89	102	78
Vapor pressure (at 20°C; hPa)	35–90	58	6.7
Enthalpy of vaporization (MJ/kg)	0.36	0.92	0.43
Flashpoint (°C)	< -20	12	35–37
Kinematic viscosity (at 20°C; (mm²/s)	0.4–0.8	1.5	3.6

Table 10.7 Properties of gasoline, butanol and ethanol

significantly higher energy content and air-fuel ratio (similar to those of gasoline) and thus an increased mileage. Butanol is well suited to existing car engines without any modifications (ButylFuel, 2009), and it can also be mixed with gasoline in any concentration, while ethanol can only be blended up to 85% with gasoline. Another problem of ethanol is its hygroscopic and corrosive nature, which requires transportation in special tanks and blending shortly before use. Butanol, in contrast, can be blended at the refinery and distributed using the existing infrastructure (pipelines, tanks, pumps, filling stations, etc.). Due to the significantly lower vapor pressure, butanol is safer to handle as well.

## 10.5.2 Butanol toxicity

Solvent toxicity proved to be the most severe limitation during the ABE fermentation process. To overcome this issue, more tolerant strains were designed (see Section 10.5) and integrated recovery techniques were applied (see Section 10.6).

While acetone and ethanol are only moderately toxic, butanol has disastrous effects on bacterial cells even at low concentrations. Already at a concentration of 1.1% (120 mM) butanol, the growth rate of *C. acetobutylicum* is decreased by 50% and at 1.5% (165 mM) butanol, growth is almost completely inhibited (Baer *et al.*, 1987; Vollherbst-Schneck *et al.*, 1984). This effect is caused by an increase in membrane fluidity (Baer *et al.*, 1987, 1989; Ingram, 1976; Vollherbst-Schneck, 1984) and inhibition of membrane proteins such as transporters (Bowles and Ellefson, 1985; Moreira *et al.*, 1981; Ounine *et al.*, 1985) and ATPases (Terracciano and Kashket, 1986).

## 10.5.3 Bacteriophage infections

Problems with bacteriophage infections emerged in almost all historical industrial ABE fermentation processes, no matter how good hygiene and plant practices were applied (Hastings, 1971; Jones *et al.*, 1986). While most bacteriophage infections manifest in similar symptoms such as decreased growth rates and poor solvent production, bacteriophages seem to be very strain specific. The most successful method to overcome the effects of bacteriophage infections proved to be strain immunization (Jones *et al.*, 1986).

## 10.6 Future trends

As already stated in the introduction, a problem that every biofuel candidate must face is the question of substrate. Competition between nutritional and transportational needs represents a major ethical problem. Although new plants have been built and existing ones reopened in Brazil and China (see Section 10.3), these are still based on sugar cane or starchy materials. In future, the possibility of converting other compounds into butanol will be becoming more and more important. One

interesting resource is lignocellulosic hydrolysates. Processes using such substrates are already used for ethanol formation (Dürre, 2007). Currently, a large number of research projects focus on this topic. Another exciting possibility is the use of synthesis gas. This mixture of mostly carbon monoxide and hydrogen can easily be obtained from biomass, thus avoiding costly pretreatments. As syngas is a common bulk material in the chemical industry, technical experience in operation of the respective equipment already exists. The proof of principle of biological butanol formation from syngas has been demonstrated (Köpke, 2009). An additional argument in favor of such a process is the direct consumption of gaseous CO and  $CO_2$ , thus helping to reduce the global greenhouse effect. It is envisaged that therefore such processes will become important industrial applications in future.

### 10.7 Sources of further information and advice

Since 1990, an international conference on the genetics and physiology of acidand solvent-producing clostridia is being held biannually. Clostridium 1 took place in Salisbury, UK, while the following meetings were located in Blacksburg, Virginia (1992), Evanston, Illinois (1994), Ulm, Germany (1996), Toulouse, France (1998), Champaign/Urbana, Illinois (2000), Rostock, Germany (2002), Edinburgh, UK (2004), Houston, Texas (2006), and Wageningen, The Netherlands (2008). Clostridium 11 will be held in the United States in 2010 and Clostridium 12 probably in Nottingham, UK in 2012. These symposia provide an excellent means for both young and experienced researchers to learn about most recent findings in basic and applied aspects of the solvent-forming clostridia.

An additional resource is the web page 'www.clostridia.net', maintained by Nigel P. Minton in Nottingham, providing information on apathogenic and pathogenic clostridia, forthcoming conferences, transnational research collaborations, and Marie Curie-workshops especially aiming at pre- and postdoctoral researchers.

Finally, six books have been published meanwhile, either dealing with specific aspects of clostridia or giving a comprehensive overview of this genus (Bahl and Dürre, 2001; Brüggemann and Gottschalk, 2009; Dürre, 2005b; Minton and Clarke, 1989; Rood *et al.*, 1997; Woods, 1993).

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# **11** Biochemical production of other bioalcohols: biomethanol, biopropanol, bioglycerol, and bioethylene glycol

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**Abstract:** Bioethanol and biobutanol are the two most commonly discussed bioalcohols for fuel purposes. However, other alcohols can be produced from biomass. This chapter will introduce other bioalcohols and discuss their production. These bioalcohols include: biomethanol, biopropanol, bioglycerol, bioethylene glycol, as well as branched chain bioalcohols and other theoretical biofuels. It will compare the advantages and disadvantages of employing different fuels on the basis of both availability and ease of production as well as chemical, biological, and physical properties of these fuels.

**Key words:** biomethanol, glycerol, biopropanol, bioalcohols, biofuel production.

#### 11.1 Introduction

When researchers think bioalcohols, bioethanol and biobutanol are the first alcohols that come to mind, because they are the most prevalent and the most frequently researched.<sup>1–4</sup> These are commonly considered the alcoholic fuels in the United States, because of the ability to produce them from corn and corn by-product, which is a large agricultural product in the Midwestern United States. However, other bioalcohols can be produced and they each have their own advantages and disadvantages which will be described below.

In general, we consider an alcohol to be a bioalcohol if it is produced from biomass. There are many forms of biomass, including: wood and wood residue; agricultural crops and waste by-products; municipal solid waste, animal waste, and sewage; waste from food processing; and algae and aquatic life.<sup>5</sup> This chapter will discuss not only the bioalcohols that can be produced from biomass, but also the traditional methods and types of biomass employed to produce the bioalcohols. This is important when considering biofuels and their use as a renewable energy source. Different countries have different biomass sources and, therefore, there will not likely be a single bioalcohol/biomass solution for renewable energy for all countries and all applications. Other issues to consider when choosing a bioalcohol fuel are the toxicity of the fuel or fuel by-products, the volatility of the fuel, and the energy density of the fuel.

#### 11.2 Biomethanol

Methanol is the simplest alcohol. It has the chemical formula  $(CH_3OH)$  and is more volatile and more toxic than ethanol. Traditionally, methanol has been considered wood alcohol, because it was produced by pyrolysis of wood. In theory, pyrolysis of wood could be considered biomethanol, because it is producing the alcohol-based fuel from a biological source (wood). However, the term biomethanol is typically used to describe methanol produced from one of two methods: Fischer Tropsch reaction of syn gas or biomethane. A common source of biomethane is landfills. The process of making biomethanol from landfill gas and syn gas is a cost-intensive chemical process. Although in theory this is a large source of energy, because current residues/waste by-products from agricultural and forest products amount to approximately one-third of the total commercial energy use.<sup>6</sup>

In general, we would break biomethanol production into three methods: syngas, bio-gas/bio-methane, and carbohydrates. Syn-gas contains carbon monoxide (~30vol%), hydrogen (25–30vol%), carbon dioxide (20–30vol%), methane (~10vol.%), and ethane (~3vol.%). Typically, purification and/or gas conditioning are needed before syn-gas can be catalytically converted to biomethanol. The catalyst used in the reactor for methanol synthesis is typically copper oxide, zinc oxide, or chromium oxide.<sup>7</sup> The two standard chemical reactions for methanol synthesis at these catalysts are shown below.

> $CO + 2H_2 \Leftrightarrow CH_3OH$  $CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$

Both of these reactions are exothermic and result in a loss of moles of gas, so Le Chatelier's principle would dictate that the reaction is favored by high pressure and low temperature. Side products can be produced and need to be considered if depending on the purification needed of the methanol product. Side products could include dimethyl ether, formaldehyde, or more complex alcohols.<sup>7</sup> These side products may decrease the energy density of the fuel as well as the toxicity.

Biogas or biomethane that is captured from landfills is often times called landfill gas. Landfill gas is typically considered to be the same as natural gas, but it is not. Natural gas is more than 80% methane and landfill gas is typically 40–60% methanol with the remaining gas being mostly carbon dioxide. The EPA predicts that each pound of biodegradeable waste in the landfill will produce 10–12 standard cubic feet of gas over a 25-year period.<sup>8</sup> This landfill gas accounts for 34% of the methane emissions,<sup>8</sup> so it is clearly a large source of methane that could be tapped for fuel purposes. The overall reaction for methanol production from landfill gas is:

$$CH_4 + H_2O \iff CH_2OH + H_2O$$

However, this process is not direct. The landfill gas is reformed to syn gas after a pretreatment to remove sulfur compounds and a compression to 400 psi and then the syn gas is reacted to methanol and purified.<sup>8</sup>

The general method for biomethanol production from carbohydrates is shown in Fig. 11.1 where carbohydrates are gasified and partially oxidized to hydrogen and carbon monoxide which is used to catalytically produce methanol via the same catalytic methanol synthesis method described above for syn gas.<sup>7</sup> Clearly, biomass is more complex than syn gas, so more pretreatment, gas cleaning, and gas conditioning is needed. In general, pretreatment involves chipping to a size below 5 cm and drying, whereas gas cleaning involves removing tars, soot, alkali metals, BTX (benzene, toluene, and xylenes), and inorganic impurities (HCl, ammonia, HCN, H<sub>2</sub>S, and COS).<sup>7</sup> Gas conditioning is involved in getting rid of the methane and other hydrocarbons in the gas as well as altering the ratios of CO:CO<sub>2</sub>:H<sub>2</sub> if necessary via the water gas shift reaction, amine stripping of carbon dioxide, or other CO<sub>2</sub> scrubbing methods. Steam reforming of methane (and other light hydrocarbons) over nickel catalysts will form carbon monoxide and hydrogen,<sup>7</sup> which then can be used directly for producing methanol. Overall, this is an area of research that appears to be the future of considering methanol as a biofuel, but currently researchers in the United States are more focused on ethanol as a fuel due to volatility and toxicity issues. Methanol also has lower volumetric and gravimetric energy density, which limits its usefulness for portable or transportation power.

### 11.3 Biopropanol

Biopropanol is a rarely discussed biofuel. Propanol is an alcohol with a three carbon chain ( $C_3H_7OH$ ). Propanol is less toxic and less volatile than methanol, so it has some interesting properties as a fuel, although it is rare to consider it a fuel,



11.1 Schematic of biomethanol production of biomass carbohydrates.

since most propanol produced is used as a chemical solvent. There are two main types of propanol, n-propanol and isopropanol. Biopropanol is n-propanol that is produced from biomass. The University of British Columbia has developed technology for producing biopropanol (as well as biobutanol and bioethanol) from syn-gas using novel catalysts. Syntec Biofuels is commercializing this technology.<sup>9</sup> The other method for producing biopropanol is from microbial fermentation of biomass (cellulose), but that is extremely inefficient, because very little propanol is traditionally produced and propanol is toxic to the cell in any significant concentration, so it is impractical at this stage of biotechnology. The issues with microbial production of biopropanol as analogous to the issues with microbial production of biopropanol will also become more feasible.

## 11.4 Bioglycerol

Glycerol is one of the frequently produced bioalcohols, because glycerol is a waste product of biodiesel production. However, glycerol is rarely considered a biofuel, because it is not easy to burn and therefore is only useful for non-combustion-based fuel uses.

Biodiesel is typically produced by the transesterification of lipids (vegetable oil, soybean oil, waste oil, etc.) with an alcohol (typically methanol). If methanol is employed, the transesterification results in the production of methyl esters, which is used as the fuel, and glycerol which is the by-product as shown in Fig. 11.2. A total of 100 kg glycerol is produced for every ton of biodiesel manufactured.<sup>10</sup> The main problem with bioglycerol is twofold: (1) it is a waste product so it is low concentration and impure and (2) there has not been a market for bioglycerol. Since glycerol is part of the waste stream, it is in low concentrations and in a highly basic aqueous environment, because the catalyst for transesterification is typically sodium or potassium hydroxide. This can be fixed by neutralization and distillation, but that is not cost effective. Secondly, glycerol is not commonly used as a fuel, because it does not burn well and cannot be easily electrochemically oxidized.<sup>11-15</sup> However, it may be useful for other chemical purposes, because it can be used to produce glyceric acid and dihydroxyacetone. It is important to note that the biodiesel process is not really producing a bioalcohol, but it is using a low energy density bioalcohol (methanol) to produce a higher energy density bioalcohol (bioglycerol), which is different than using carbohydrates to produce bioalcohols.

## 11.5 Bio-ethylene glycol

Ethylene glycol is similar in structure to glycerol. Glycerol is a C3 triol and ethylene glycol is also a polyol, but a C2 diol. Although ethylene glycol has two alcohol groups, its main application is as the main ingredient in antifreeze and not



11.2 Schematic of transesterification process.

for fuel purposes. Although it can be used, similar to glycerol, as a fuel for a fuel cell.<sup>13,16</sup> Ethylene glycol is normally produced from ethylene which is produced from fossil resources rather than biomass. However, ethylene glycol can be produced from biomass. Ethylene can be produced from sugars via microorganisms like *Pseudomonas syringae* and *Penicillium digitatum*. The bio-ethylene produced can then be used to produce ethylene glycol. However, ethylene glycol can also be produced by pyrolysis of biomass.<sup>17</sup> Although ethylene glycol is toxic, it is easy to work with due to its low volatility and other solvent properties, so it is easy to reform and quite high in energy density. It has also been proposed that ethylene glycol can be produced from biomass like cellulose and xylan by periodate oxidation followed by reductive hydrolysis. This was shown to be successful for producing bio-ethylene glycol directly from corn residue without any isolation or purification processes.<sup>18</sup>

## 11.6 Other possible bioalcohols

The above described bioalcohols are the most commonly discussed for fuel purposes, but they are not the only bioalcohols that can be produced. The procedure described above for producing bio-ethylene glycol from corn residue can be modified to produce erythritol and xylitol.<sup>18</sup> These are not common alcohols, but there are more common alcohols that can be produced from biomass. One prime example is propanediol. There are two main forms of propanediol: 1,2-propanediol, which is also called propylene glycol, and 1,3-propanediol. 1,2-propanediol can

be produced from hydrogenating of biologically derived lactate or lactic acid.<sup>19</sup> 1,2-Propanediol can also be produced from hydrogenolysis of glycerol with Raney Nickel.<sup>20</sup> Although it has not yet been used as a fuel, it is used as a less toxic antifreeze as well as an additive for many commercially available pharmaceutical and cosmetic products. 1,3-Propanediol can enzymatically be produced from bioglycerol.<sup>21</sup> Both 1,2- and 1,3-propanediol can be produced by hydrolysis of biomass and then fermentation of the resulting sugars.<sup>21</sup> This can also be used to produce butanediol.<sup>21</sup> Although it has not been used directly as a fuel, it has been reacted further to produce an octane booster for gasoline. It is important to note that these rare bioalcohols are not currently being researched for fuels, but as we get more serious about renewable energy, we will start focusing on different fuels from different biomass sources for different applications, as needed.

Branched alcohols have also been considered as potential biofuels. Biobutanol researchers have found that they can produce branched alcohols as well. Synthetic biology has allowed for the production of isobutanol in metabolically engineered bacteria with glucose as a carbon source.<sup>22</sup> This process diverts 2-ketoacid metabolic intermediates into aldehydes via 2-ketoacid decarboxylase and then to an alcohol via alcohol dehydrogenase. This novel method for producing branched chain alcohols has also been shown to be able to produce 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-phenylethanol and has been licensed to Gevo (Pasadena, CA), which is focusing on commercialization of the technology.<sup>23</sup>

## 11.7 Advantages and limitations

It is difficult to compare the bioalcohols. Each bioalcohol has its advantages and disadvantages. For instance, bioglycerol is non-toxic, has a high energy density, and has low volatility, but it does not combust well and it has a high viscosity. Biomethanol, on the other hand, has low viscosity and is easily combustible, but is very toxic, has lower energy density than the other bioalcohols, and is very volatile. Therefore, in comparing the bioalcohols discussed above and in other chapters of this book, it is important to consider the application for bioalcohols. If safety is a primary concern, then bioalcohols like bioglycerol and bioethanol will be good choices. If low volatility is important, then bioglycerol and bio-ethylene glycol will be good choices. However, if ability to easily pump the bioalcohol is important for the application, biomethanol, bioethanol, and biopropanol will be obvious choices. If energy density is important (transportation and air applications), then high energy density will result in considering bioglycerol and bioethylene glycol.

## 11.8 Conclusions and future trends

As we focus on mitigating global climate change and replacing petroleum as our transportation energy source, more and more alternative and renewable energy strategies will be considered. Bioalcohols are one important alternative energy strategy. Although bioethanol and biodiesel seem most economically and scientifically feasible today, other biofuels will be considered, especially bioglycerol, biomethanol, and branched longer chain bioalcohols as we move forward at developing energy strategies for future generations. Although many bioalcohols will likely to be studied over the next two decades, biomethanol is the bioalcohol other than bioethanol that is probably closest to commercialization and feasibility. However, the technology for producing branched chain bioalcohols has been licensed to a commercial company (Gevo) and the technology for producing biopropanol has been licensed to Syntec Biofuels. Therefore, commercially produced future bioalcohols in the United States and other countries will probably not be limited to bioethanol.

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## Production of biogas via anaerobic digestion

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Abstract: Anaerobic digestion is a biological process that converts the organic matter present in various types of wastes (sewage sludge, agro-industrial wastes, OFMSW, energy crops) into: (1) biogas (rich in methane, suitable to be used for heat and/or electricity generation) (2) biosolids (microorganisms grown on the organic matter and unconverted particulate residues mostly fibres which can be used as soil conditioner), and (3) liquor (dissolved organic matter, recalcitrant to anaerobic degradation and nutrients, which may be used as liquid fertiliser). The vast improvement in various scientific fields (reactor engineering, modelling and control practices, molecular tools) helped to gain a better insight of the process. In addition, the policy to promote biogas utilisation contributed in boosting the application of the anaerobic digestion technology to achieve a two-fold goal: energy production and waste minimisation. All these aspects are discussed in what follows.

Key words: anaerobic digestion, biogas, control, modelling, utilisation.

#### 12.1 Introduction: the anaerobic digestion process

Anaerobic digestion is a biochemical process conducted by the concerted action of a consortium consisting of several groups of microorganisms that degrade the organic matter into a gaseous mixture consisting of methane and carbon dioxide (biogas) in the absence of oxygen. It happens naturally in environments with lack of oxygen such as the bottom of lakes, swamps, the landfills or the intestine of animals. However, the term 'anaerobic digestion' usually describes the technology of accelerating the naturally evolved bioprocess in an artificial environment of a closed vessel.

Anaerobic digestion was first applied in the tenth century BC for heating bath water in Assyria. In the seventeenth and eighteenth centuries, a flammable gas mixture produced was correlated with the decay of organic matter and, moreover, the correlation became quantitative; the more organic matter is decayed, the more flammable gas is produced. It was in 1808, when Sir Humphrey Davy discovered that methane was a constituent of the gas produced by cattle manure. The anaerobic technology was first demonstrated in Bombay, India, in 1859, by building an anaerobic digester (Meynell, 1976). The biogas recovered from a sewage treatment plant was used to fuel street lamps in Exeter, England, in 1895 (McCabe, 1957). The development of microbiology science in the 1930s brought up further improvement in the anaerobic technology through identification of the anaerobic bacteria, and the conditions favouring the process efficiency and the limitations

(Buswell and Hatfield, 1936). Since then, numerous anaerobic applications have been developed worldwide, mainly in the field of waste treatment, but also in manufacturing of chemicals, fibres, food, etc.

## 12.1.1 The process

Anaerobic digestion is a complex bioprocess consisting of successive, often interactive steps carried out by groups of microorganisms with different growth rates and sensitivity to environmental conditions (pH, partial pressure of hydrogen, etc.). The process can be outlined as consisting of the following steps (Fig. 12.1):

- Disintegration: The complex particulate waste disintegrates to organic polymers such as carbohydrates, proteins and lipids. Disintegration lumps a number of steps such as lysis, non enzymatic decay, phase separation and physical breakdown (e.g. shearing; Batstone *et al.*, 2002).
- Hydrolysis: The organic polymers (carbohydrates, proteins and fats) are hydrolysed (depolymerised) by extracellular enzymes to their respective monomers (sugars, amino acids, lipids), which can be taken up by the microorganisms for further degradation. In the case of particulate complex organic matter consisting of lignocellulosic material (mainly of plant origin),



*12.1* COD flux for a particulate waste consisting of 10% inerts and 30% each of the main organic polymers (in terms of COD) (Batstone *et al.*, 2002).

pretreatment steps are necessary to enhance hydrolysis by rendering the substrate matrix more amenable to enzyme attack.

- Acidogenesis: A versatile group of microorganisms are able to convert the simple monomers to a mixture of volatile fatty acids, alcohols and other simpler organic compounds. This step is also often called fermentation. During acidogenesis, large amounts of carbon dioxide are produced as well as hydrogen. Especially in the case of sugars fermentation, the amount of hydrogen produced can be high and may be harvested for energy recovery. The growth rate of acidogens is quite high (doubling time of the order of one hour or even less) and low pH resistant (5–6) giving them the advantage of prevailing in the anaerobic consortium at adverse conditions. As a result of the rapid acid formation, there is a danger of acid accumulation (and concomitant pH drop) if the acids are not degraded in time in the steps that follow.
- Acetogenesis: The higher volatile fatty acids (propionate, butyrate, valerate, etc.) as well as the other organic molecules produced in the acidogenesis step are transformed to acetic acid, carbon dioxide and hydrogen by the acetogenic bacteria. This step is thermodynamically inhibited by hydrogen, meaning that, unless hydrogen is depleted by the hydrogen-consuming bacteria in other steps, there is an accumulation of mainly propionic and butyric acid. The acetogenic bacteria are slow growing microorganisms doubling time of the order of days.
- Methanogenesis: There are two distinct groups of microorganisms that produce methane and carbon dioxide: (1) the acetoclastic methanogens that grow on acetic acid and produce approximately 70% of methane in the biogas, and (2) the hydrogen utilising methanogens that consume hydrogen and carbon dioxide. The methane content of biogas depends on the oxidation state of the organic carbon in the initial substrate (ranging from -4 for methane to +4 for carbon dioxide); the more reduced the initial substrate is, the more methane will be produced, but on average the biogas contains 60% of methane. Acetoclastic methanogens are slow growing microorganisms (doubling time of the order of days) and are particularly sensitive to a number of factors such as pH, lack of nutrients, certain compounds, etc.

## 12.2 Factors affecting the anaerobic digestion process

The anaerobic consortium consists of several microorganism groups with different physiology that coexist syntrophically or antagonistically, resulting in a different response to environmental changes. As a consequence, when the activity of one of the microorganism groups is inhibited, the growth rates of other microorganisms are affected, changing the population balance, often causing a decrease in process efficiency or even failure. It has been recognised that the most important factors affecting the anaerobic digestion process are the pH, the temperature, the nature of the feedstock (composition, nutrients), the presence of toxic or inhibitory substances and the organic loading rate.
### 12.2.1 The pH

The pH affects the dissociation of weak acids and bases, and therefore, the formation of undissociated acids and bases which can easily penetrate the cellular membrane changing the internal pH of the cells. The pH also influences the function of the extracellular enzymes and has an impact on the hydrolysis rate. In most cases, the anaerobic transformation of organic matter is achieved most efficiently at a neutral pH. Many species though can grow at lower or higher pH values.

Low values of pH and the concomitant intermediate acid accumulation are more inhibitory to the methanogens than the acidogenic bacteria. Acidogens can grow and continue to produce acids at low pH values (5–6), intensifying the inhibitory conditions to the methanogens. However, it is known that methanogenesis can occur in extreme environments where very low or high pH values prevail such as swamps, hot springs, etc.

It is common to the acidogens that produce a mixture of metabolic products to switch their metabolism towards the formation alcohols to avert any further pH decrease (Huang *et al.*, 1986; Gottschal and Morris, 1981; Lowe and Zeikus, 1991).

# 12.2.2 Temperature

As temperature increases, the biochemical reactions take place at a higher rate, up to a point where the structure of the cellular components (proteins, nucleic acids, etc.) change, rendering the cell inactive. Generally the microorganisms are distinguished into three groups according to the temperature range in which they grow: thermophilic (optimum above 50°C), mesophilic (optimum 30–40°C) and psychrophilic (optimum below 20°C). The enzymes developed in a microorganism, after proper adjustment, can be tolerant to temperature changes. As a result there are bacteria that can grow in more than one temperature range. In the majority of anaerobic systems, the acetoclastic methanogens, being the most sensitive microorganisms group in anaerobic digestion, are influenced dramatically by small changes in temperature. Temperature in combination with other factors influences the number of bacteria that coexist in heterogeneous populations, and as a result, it has a significant part in the selection of the microorganisms' group that will prevail in an anaerobic digestion system.

Mesophilic and thermophilic anaerobic digestion are preferred against psychrophilic due to the higher rate of the process at these temperature ranges. However, psychrophilic temperatures are often imposed by local climatic conditions and it is important to improve the process in these conditions. Most research has focused on mesophilic bacteria acclimated to low temperatures and not on real psychrophilic bacteria isolated from naturally cold habitats (Kashyap *et al.*, 2003).

### 12.2.3 Feedstock composition

Anaerobic bacteria can degrade a variety of organic compounds (carbohydrates, proteins, lipids, etc.). The methane content of the biogas mixture depends on the oxidative state of carbon in the compounds present in the feedstock; the more reduced the carbon is, the higher the content of biogas in methane is (Gujer and Zehnder, 1983). The feedstock should also be balanced with respect to the ratio of carbon and nitrogen (C:N = 20:30), since the microorganisms use carbon and nitrogen at this ratio range. Quite often, organic feedstocks contain these nutrients at lower or higher ratios. In such cases, the codigestion of selected feedstocks can adjust the required balance ('diet') and enhance biogas production, e.g. codigestion of sewage sludge with agricultural wastes or municipal solid wastes (Alatriste-Mondragon et al., 2006) as well as cattle manure with municipal solid wastes (Hartmann and Ahring, 2005). Apart from C and N, other elements present at trace concentrations are also crucial to the growth of anaerobic microorganisms. For example, Ni (involved in the synthesis of coenzyme F430), Fe (constituent of electron carriers), Mg (stabilising the cellular membranes), Ca (stabilising the cellular wall and contributing to the thermal stability of the endospores), Co (component of the vitamin B<sub>12</sub>), Zn (constituent of several enzymes). etc. If these trace elements are not contained in the feedstock, they should be supplied since their absence is correlated with decrease in efficiency (Zandvoort et al., 2006).

### 12.2.4 Toxic compounds and inhibitors

Oxygen: The tolerance of the microorganisms in relation with oxygen classifies them as aerobic (when growth requires oxygen), facultative anaerobes (when growth may occur on oxygen when available but does not require it) and anaerobes, classified further to strictly anaerobes (when oxygen is toxic) and aerotolerant anaerobes (when growth may occur in the presence of oxygen but without utilising it). Strict anaerobes include Clostridia, methanogens, sulphate reducers and homoacetogens. The sensitivity to oxygen varies widely among the strict anaerobes. All bacteria contain enzymes to react with oxygen and produce toxic free radicals that destroy vital cellular components. However, it is the presence of other enzymes that remove the toxic oxygen radicals that determine the degree of tolerance to oxygen. In anaerobic environments the traces of oxygen are rapidly consumed by the facultative anaerobes of the consortium, decreasing the redox potential to acceptable levels (-400 mV). For this reason, the facultative anaerobes are usually found in external layers in systems where spatial distribution of the various populations is possible (e.g. lagoons, heterogeneous or hybrid bioreactors).

Ammonia: It is the degradation product of nitrogenous compounds such as proteins and amino acids. Anaerobic digestion of feedstocks such as manure results in the production of high amounts of ammonia. Non-ionised ammonia is quite inhibitory to methanogens. Since the concentration of non-ionised ammonia is a function of pH, the inhibition is less at neutral pH. There are contradictory reports on the levels of tolerance to ammonia, due to differences in substrates, inocula, environmental conditions and acclimation periods. The inhibitory total ammonia concentration causing a 50% decrease in the methane production ranges from 1.7 to 14 g/L (Chen *et al.*, 2008). Acclimation plays a significant role in making the anaerobic consortium tolerant to high levels of ammonia (Bhattacharya and Parkin, 1989; Angelidaki and Ahring, 1993).

Long chain fatty acids (LCFAs) and other organic compounds: LCFAs tend to be adsorbed on surfaces and interfere with the molecule transfer mechanisms or the protection functions of the cell wall or membrane. Moreover, flotation of biomass can occur as a result of the adsorption of LCFA (Rinzema *et al.*, 1989). The inhibition of LCFA in thermophilic anaerobes is more severe because of the different composition of their cell membranes (Hwu and Lettinga, 1997). Biodegradation of LCFAs, although difficult, has been observed in mesophilic and thermophilic conditions.

Other organic compounds which have been found to be toxic to anaerobic digestion are: alkyl benzenes, halogenated benzenes, nitrobenzenes, phenol and alkyl phenols, halogenated phenols, nitrophenols, alkanes, halogenated aliphatics, alcohols, halogenated alcohols, aldehydes, ethers, ketones, acrylates, carboxylic acids, amines, nitriles, amides, pyridine and its derivatives (Chen *et al.*, 2008). The extent of toxicity depends on several factors such as the toxicant concentration, microorganism concentration, toxicant exposure time, cell age, feeding pattern, acclimation and temperature (Yang and Speece, 1986).

Metals: They can be distinguished into light and heavy metals. Light metals are present in the form of cations in solution and, in the case of anaerobic digesters, they usually include sodium, potassium, calcium and magnesium. They are usually added in the form of chemicals for pH control, but they can also arise from the breakdown of biomass. They are required for microbial growth at moderate concentrations, but they can cause severe inhibition or even toxicity at high concentrations (Soto *et al.*, 1993).

Heavy metals (e.g. chromium, iron, cobalt, copper, zinc, cadmium and nickel) can be present in significant concentrations in municipal sewage and sewage sludge as well as in industrial wastewaters. Several metals such as iron, zinc, nickel, cobalt, molybdenum and copper are constituents of vital enzymes. Due to the non biodegradability of heavy metals, they tend to biosorb and accumulate at toxic concentrations. Apart from sorption, the heavy metals may be precipitated (reacting with sulphide, carbonate or hydroxyls) or form complexes in solution with degradation compounds produced during digestion. However, only metals in soluble free ionic form exhibit toxicity (Mosey and Hughes, 1975; Oleszkiewicz and Sharma, 1990). Therefore, immobilisation of heavy metals can take place through processes such as precipitation, sorption and chelation. The relative sensitivity of acidogenesis and methanogenesis to heavy metals is Cu > Zn > Cr > Cd > Ni > Pb and Cd > Cu > Cr > Zn > Pb > Ni, respectively (Lin, 1992, 1993).

Sulphide and sulphate: The presence of sulphate in the absence of oxygen causes anoxic conditions since it can be used as an electron acceptor instead of oxygen. The sulphate reducing bacteria can utilise a number of substrates (acetate, hydrogen, propionate, butyrate) in anaerobic systems and, therefore, they compete with the groups of microorganisms that degrade the same substrates. As a result the flow of electrons is diverted mostly to sulphide instead of methane production reducing the efficiency of the anaerobic systems (in terms of biogas production).

Sulphide is toxic to methanogens but also to the sulphate reducing bacteria. There is a great discrepancy in the literature concerning the mechanism of inhibition and the toxicity levels of sulphides (Chen *et al.*, 2008). Sulphide removal can take place through stripping, coagulation, oxidation, precipitation but also through biological processes such as oxidation to sulphur (Oude Elferink *et al.*, 1994; Song *et al.*, 2001). Acclimation to sulphide can also be beneficiary to methanogens, increasing their tolerance levels.

### 12.3 Advantages and limitations

The most profound advantage of anaerobic digestion is the production of a methane rich gas which can be used to produce energy (Fig. 12.2). Since the feedstock for anaerobic digestion is renewable and does not deplete any fossil resources, the energy recovery from the produced biogas does not add to the atmospheric carbon. Moreover, utilisation of the digestate as fertiliser reduces the need to produce inorganic fertilisers and, therefore, reduces further the fossil fuel consumption required for their production (Fig. 12.2). As a result, there are microas well as macro-economic benefits through energy and fertiliser substitution as well as operation of decentralised anaerobic digestion plants.

The other important advantage of anaerobic digestion is related with the reduction of the organic load of wastes that if released in the environment would cause land and water pollution. The hygienic aspect is also very significant, since pathogens are reduced especially under thermophilic conditions. Odour control is also important. Odour causing compounds are consumed in the sealed anaerobic digesters. Fly propagation (major problem especially in the case of manure) is also limited.

Methane is a major greenhouse gas and its release in the atmosphere poses serious environmental problems. A well-managed anaerobic digestion scheme should minimise the overall emissions while maximising the biogas produced. Since methane is a much more undesirable greenhouse gas than carbon dioxide, it should be burned in a flare, even if its burning is not used for energy production.

It should be made clear though that anaerobic digestion does not eliminate the wastes but renders them easier to manage further on via other processes such as composting, aeration treatment, mechanical separation, etc. In the case of municipal wastewater treatment a number of post treatment methods have been suggested (Chernicharo, 2006).



12.2 Utilisation of anaerobic digestion products.

Anaerobic digestion is a complex microbial process susceptible to a number of environmental factors that increase the risk of process failure. The variable nature of the feedstock during the year may be a problem too; more organic kitchen wastes are produced during the summer, while pruning and woody materials prevail during autumn. Although there are very low cost digesters that have been used in farms (especially in developing countries), the cost of this technology increases if reliability and high efficiency are required; sophistication of the systems through elaborate bioreactor design, application of advance monitoring and control schemes or employment of trained personnel raises the cost significantly.

Another major drawback of anaerobic digestion is the long start-up period required. During start-up, the anaerobic systems cannot yield satisfactorily. The duration of start-up is affected by the composition and the organic load of the waste, the volume, activity and adjustability of the inoculum, several environmental factors (temperature, pH, nutrients, etc.) and operating parameters (hydraulic retention time, mixing) as well as the bioreactor configuration (Weiland and Rozzi, 1991). Utilising a pair of anaerobic digesters instead of a single one secures the incessant operation of the anaerobic plant; if one of the digesters has poor efficiency or becomes sour due to mishandling or other reasons, the other digester can be used at its full capacity and, furthermore, to provide an activated, adjusted inoculum that could shorten the recovery of the start-up time of the first digester.

# 12.4 Process integration for biogas production

The main parameters for consideration in the process integration are the feedstock, bioreactor configurations and methods for enhancing the process efficiency.

# 12.4.1 Feedstock

The range of organic matter types that can be subjected to anaerobic digestion is wide; from low organic load wastes such as municipal sewage to high organic load wastes (such as the organic fraction of the municipal solid wastes). Specifically, the industrial sector (e.g. breweries, sugar mills, distilleries, food-processing industries, tanneries, and paper, pulp industries) generate large amounts of organic wastes. Food products and agro-based industries contribute 65–70% of the total industrial wastewater in terms of organic load (Zafar, 2008). The term 'residues' is often preferred to 'waste' whenever possible, in order to assign a value of exploitable resource to the organic matter rather than being a problem to be solved. The term 'feedstock' is also often preferably used to describe the material fed to a digester.

Feedstocks with a high biomethane potential can be classified as follows:

- Agricultural (livestock manure, agricultural residues, animal mortalities, energy crops)
- Industrial (wastewater, sludges, by-products, slaughterhouse waste, spent beverages, biosolids)
- Municipal (sewage sludge, organic fraction of municipal solid waste)

A database including the biochemical methane potential of various feedstocks can be found at the website (http://www.emu-bioconversion.eu/). Data are collected (but not validated) from literature and, after standardisation of the units, the chemical composition and the methane potential of various feedstocks are included in the database.

# 12.4.2 Anaerobic digesters

The anaerobic continuous stirred tank reactor (CSTR) is the most basic bioreactor configuration. The major advantage of the CSTR is its simplicity in construction and operation. However, large bioreactor volumes are required to provide the high retention time necessary to sustain the slow growing anaerobic microbial mass inside the bioreactor, which raises the cost of the process. Therefore, for an efficient anaerobic system with relatively small bioreactor volume, the design of anaerobic digesters should aim at providing an optimum environment for the growth of the anaerobic microorganisms given the complexity of their physiology and the syntrophic and/or antagonistic interactions among them. Lettinga (1995) specified certain criteria:

- High retention of the active biomass (microorganisms) inside the bioreactor.
- Sufficient contact between the biomass and the substrate.
- High reaction rates and elimination of the limiting transport phenomena.
- Suitable environment for the adaptation of the biomass to various types of feedstocks.
- Suitable environment for all organisms under the operating conditions.

Depending on the solid content of the feedstocks, different bioreactor configurations can be used:

- Low solid content feedstocks (e.g. secondary wastewater treatment, wastewater from food industry, hydraulic flush manure systems; swine)
  - Anaerobic lagoons fixed, floating, or submerged covers
  - Completely mixed reactors
  - Anaerobic filter reactors
  - Fluidised bed reactors
  - Upflow anaerobic sludge blanket reactors (UASBR)
  - Anaerobic baffled reactors (ABRs).
- Medium solid content feedstocks (e.g. dairy manure, 'scraped' swine manure, municipal or food industries sludge)
  - Plug flow reactors
  - Completely mixed reactors
  - Contact reactors.
- High solid content feedstocks (e.g. organic fraction of municipal solid wastes, agricultural residues, food processing waste; food residuals; pulp-paper sludge)
  - Plug flow
  - Completely mixed
  - Leach-bed.

A brief description of the main bioreactor types follows:

• Fixed-bed anaerobic reactor (anaerobic filter): The wastewater is introduced from the bottom or the top of a column which is filled with inert material (rocks, cinder, plastic or gravel). The filling material provides the surface upon which microorganisms are attached forming a biofilm. The microorganisms can also be retained through entrapment in the micro-porous structure of the filling material. Clogging is a typical problem with this type of digester. The organic load of the wastewater must be low to medium. Recirculation must be applied so that the organic load in the entrance is maintained between 8 and 12 g/L. Wastewaters containing significant amounts of suspended solids or constituents that cause precipitation of organic and inorganic compounds are not suitable for this bioreactor type. The filling material must provide large void space to avoid clogging (95%) and have large specific surface (100–200 m<sup>2</sup>/m<sup>3</sup>).

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- Expanded and fluidised bed anaerobic digester: This type of configuration allows a more effective mass transfer from the liquid phase to the membrane, because fine filling material is used (0.2–0.5 mm). The upflow velocity must be high enough (through recirculation) to maintain the expansion of the bed between 15% and 30%, while if the expansion raises up to 300%, the bed is characterised as fluidised (Hall, 1992). Energy consumption required to provide recirculation is the main disadvantage of this bioreactor. The wastewater must contain low suspended solids as in the case of the fixed bed bioreactors.
- UASBR: The UASBR was designed as an alternative to wastewater treatment without the operating problems of bioreactors with filling materials but incorporating the concept of biomass immobilisation (Lettinga et al., 1980). In this bioreactor type, the microorganisms are agglomerated to form a dense structure (granule) with excellent settling properties and strength under adverse conditions. The granular sludge blanket remains in the bottom of the bioreactor. The feed is introduced from the bottom and the motion of the flow is upwards. The upflow velocity is very important since it influences the formation of the granules. Typical upflow velocities range between 0.5 and 3 m/h (Annachhatre, 1996). The biogas produced is often entrapped in the granules making them lighter and buoyant with their potential wash out. An effective three phase separator on the top of the bioreactor results in the retention of the granule and their return to the sludge blanket. UASBR is a reliably tested technology for the treatment of a wide range of wastewaters (from municipal wastewater to high strength agro industrial wastewater) with low solid content. It has low installation, operation and maintenance costs. More than 900 full-scale units are currently being operated all over the world (Garcia et al., 2008). Hybrid systems have been developed to combine the characteristics of a UASBR and an anaerobic filter, expanded or fluidised bed reactor. Hybrid UASBR have been used to treat a variety of industrial wastewaters over the years (Banu and Kaliappan, 2008; Sunil Kumar et al., 2007; Ramakrishnan and Gupta, 2006; Sandhya and Swaminathan, 2006).
- ABR: It is a rectangular tank with baffles. The wastewater flows above and below a series of baffles successively coming into contact with the biomass which is accumulated in the bottom of the bioreactor (McCarty and Bachmann, 1992). This bioreactor type is simple in structure, with no moving parts or mixers. The biomass is not necessary to have good settling properties as in the UASB, in order to be retained in the bioreactor. It is an efficient system at low retention times and its operation is stable under sudden changes in the organic loading rate (Barber and Stuckey, 1999). A modification of this bioreactor type led to the periodic anaerobic baffled reactor (PABR) which is based on the periodic feeding mode to all compartments. In PABR, the switching frequency of the feed allows flexibility in operation; the PABR can be operated as a simple ABR, if the switching frequency is set to zero, and, in the

extreme case of very high switching frequency, as a single-compartment upflow bioreactor (Skiadas and Lyberatos, 1998; Stamatelatou *et al.*, 2009).

- Plug flow: It is a long narrow insulated and heated tank. The digested material flows from one end of the tank to the other as fresh feedstock enters the bioreactor. The bioreactor can be placed horizontally or vertically. It is used in the case of solid feedstocks. In order to provide mixing, various practices are applied (de Baere, 2008). In the Dranco process (vertical, downflow plug flow digester), the fresh feedstock is mixed with a portion of the digested material and is introduced from the top of the bioreactor. The same concept can be applied while the plug flow reactor is placed horizontally (Kompogas process). In this case slowly rotating impellers inside the reactor can aid the horizontal movement of the mixture, also serving for mixing, degassing and suspension of the heavier particles. In another plug-flow type configuration (Valorga process), the horizontal flow is circular and biogas injection at intervals under pressure through a network of nozzles provides mixing.
- Leach bed: The feedstock is loaded in a vertical bioreactor to form a bed through which a liquid stream percolates as a leachate and is recirculated to the top of the same reactor where it is produced (Biocel process). This process is implemented in Lelystad, The Netherlands (ten Brummeler, 1999).
- Complete mixed anaerobic digester anaerobic contact process. It usually consists of a round insulated tank, above or below ground. Heating is provided through coils with hot water inside the tank or an external heat exchanger. Mixing is achieved through a motor driven mixer, recirculation of the mixed liquor or biogas. The cover can be floating or fixed. In the case of low solid content feedstocks and in order to enhance the biomass concentration in the bioreactor, a modification of the complete mixed anaerobic digester led to the anaerobic contact process. In this configuration, the bioreactor is followed by a settling tank (or inclined parallel plates, membranes, etc.; Defour *et al.*, 1994) to separate the sludge from the supernatant. The sludge is recycled to the bioreactor increasing the biomass concentration.
- Covered anaerobic lagoon: It is a large earthen impoundment, lined with appropriate geomembranes and covered with a flexible or floating gas tight cover. They are used mostly for manure treatment. No heat and mixing are provided, therefore the ambient temperature is prevailed making this type of digester unsuitable in cold climatic conditions.

There are more parameters according to which an anaerobic system can be characterised:

1 Temperature of operation: All digesters usually operate within two temperature ranges, either at 35–40°C (mesophilic) or 50–60°C (thermophilic). Mesophilic anaerobic digestion is applied for digesting rumens of animals and feedstock from industrial and farm activities, while thermophilic anaerobic digestion is more suitable for sanitation of pathogen-bearing feedstocks. Another advantage of thermophilic anaerobic digestion is the fast conversion rates of the feedstock (induced by the fast metabolism of the microorganisms due to the high temperature) and, consequently, the lower retention time (and reactor volume) required. However, the psychrophilic range of temperatures ( $<20^{\circ}$ C) have also been studied, especially in lagoons and swamps. Thorough studies on reactor design and in-depth parametric analysis for psychrophilic consortia are lacking. It has been acknowledged, however, that, in psychrophilic conditions, systems favouring biomass accumulation are required to secure high efficiency (Kotsyurbenko *et al.*, 1993; Lettinga *et al.*, 2001). Another possibility has been to apply genetic engineering in the attempt to introduce stable enzymes, active in cold temperatures to give improved catalysts for the biomethanation process (Kashyap *et al.*, 2003).

- 2 Solid content of digesting mixture: When the solid content of the digesting mixture is less than 3–4% (little or no suspended solids), then the digesters are usually a single phase liquid system. Digesters treating solids are characterised as wet or dry depending on whether the solid content is up to 12–15% or more. Wet anaerobic systems are in a slurry form and can still be mixed through agitation, while for the dry anaerobic systems, the plug-flow type digesters are most suitable.
- 3 Number of bioreactors: The anaerobic systems may consist of a single bioreactor or a combination of bioreactors of different or the same design. Especially, in the case of anaerobic digestion of solid or slurry feedstocks, the use of more than one bioreactors is a common practice. Typically, two stages are used, with the first one being the hydrolytic-acidogenic step and the second one being the methanogenic step. In a two-stage process, it is possible to optimise the operational conditions of both steps since they take place in different bioreactors. The application of this concept has resulted in a great variety of two-stage configurations. The main advantage of the two-stage systems is the process stability in the case of feedstocks that would cause an unstable performance in single stage systems.

Two or three bioreactors of leach-bed type may be used in series, as in the sequential batch anaerobic composting (SEBAC) process (Chynoweth *et al.*, 1992, 2006). Leachate is transferred from a 'mature' bioreactor to a bioreactor filled with the fresh feedstock and recycled to the top of the 'mature' bioreactor until methanogenic conditions in the first stage prevail. Then, the bioreactor is switched to internal leachate recirculation until methanogenesis is completed. The volatile fatty acids from the first stage are transferred through the leachate into the 'mature' bioreactor with active methanogenic populations, while microbes from the second 'mature' bioreactor are recycled to the first one, enhancing its microbial activity.

In a similar concept, another configuration also uses batch loading to stimulate rapid volatile fatty acid production in a two-stage system. It combines one or more high solid bioreactors of leach-bed type in the first stage with a high rate and low solids bioreactor (such as an anaerobic filter or a UASBR) in the second stage (Zhang and Zhang, 1999; Lehtomäki *et al.*, 2008). The high-solids reactors are loaded and the leachate from the batch reactors is continuously circulated through a single low-solids digester. The effluent of the second bioreactor, with reduced organic load and high alkalinity, is pumped back to the first stage bioreactor(s).

Temperature phased systems is another case of multistage configuration with each stage operating at a different temperature. This process has been implemented most often using thermophilic digestion (with a temperature range of  $45^{\circ}$ C to  $65^{\circ}$ C) as the first phase, followed by mesophilic digestion (with a temperature range of  $25^{\circ}$ C to  $42^{\circ}$ C). This is designed to produce a final product with a minimal odour level, better dewatering properties and low content in pathogens.

- 4 Continuous or batch mode of operation: There are systems that operate in a continuous mode, while others are loaded in batches and, upon completion of the waste degradation up to a degree, are emptied and left with a 10–15% of the digested content as a seed for the next cycle of batch (sequencing batch reactors).
- 5 Small or large scale systems: Anaerobic digestion has been extensively applied in agriculture at small scale in the form of on-farm digesters, and the produced biogas is utilised for heat as well as electricity production. The solid and liquid residues from the anaerobic digesters can be recycled in the farm. The digesters are constructed as simple as possible in order to be economic. They are heated containers, shaped like silos, troughs, basins or ponds and may be placed underground or on the surface. They may be batch type (much simpler to construct and maintain) or continuous type. On-farm digesters usually operate at a mesophilic range of temperatures at a typical retention time of 10–30 d.

However, operation of large scale systems have the advantage of being more economically profitable; integrated farm waste management takes all factors into account (feedstock, products) with the aim of maximising the economies of scale and of eliminating the impacts to the environment. Moreover, very large scale anaerobic digestion plants, the so-called 'centralised anaerobic digestion plants', have been developed to use feedstock from a variety of sources. The primary source of feedstock is farm wastes, but also other non-toxic types of wastes, such as those coming from food processing industries or the organic fraction of the source-sorted municipal solid wastes, can be introduced in a centralised anaerobic digestion (CAD) facility. The anaerobic digesters may be either mesophilic or thermophilic and operate at typical retention times of 12–20 d. Process control schemes are usually applied in this scale since it is affordable to employ trained staff. Farmers may have an additional income through tipping fees by providing the feedstock to a CAD, but they may also benefit more through applying the

digestate on their farms as a fertiliser. The location of CAD plants is also crucial and they usually serve either a single large farm or several farms within a radius of about 10 km.

# 12.4.3 Methods for enhancing the efficiency of anaerobic digesters

The feasibility of anaerobic digestion application comes through enhancing the efficiency of anaerobic digesters. In the case of solid feedstocks, this task is challenging, since the rate limiting step has been recognised to be the disintegration and the hydrolysis of the particulate organic matter. Some of the studied methods for enhancing the biogas production are:

Pretreatment methods: They are applicable mainly when high solid feedstock is involved. In general, pretreatment methods can be divided into three main types according to the means used for altering its structural features: mechanical, physicochemical and biological. Mechanical pretreatment is almost always applied before any other kind of pretreatment, and actually refers to milling, through which reduction of particle size of solids is achieved. The reduction in particle size leads to an increase of available specific surface. Both physicochemical and biological pretreatment methods may enhance biodegradability, but physicochemical pretreatment, the feedstock is exposed to acid, alkaline or oxidative conditions, at ambient or high temperature. The use of high temperatures without the addition of some chemical agent, called thermal pretreatment, can also be used. Combinations of two or more physical and chemical pretreatment methods are also possible, such as acid-catalysed steam explosion, ammonia fiber explosion (AFEX) and CO<sub>2</sub> explosion.

For lignocellulosic feedstocks, steam pretreatment, lime pretreatment, liquid hot water and ammonia based pretreatments seem to have high potential (Hendriks and Zeeman, 2009). The main effect of these methods is to dissolve the hemicellulose and alter the lignin structure, improving the accessibility of the cellulose to hydrolytic enzymes. In the case of municipal activated sludge, the goal of pretreatment is to rupture the cell wall and to facilitate the release of intracellular matter in the aqueous phase for subsequent degradation and enhance dewaterability. Various pretreatment methods have also been studied (Weemaes and Verstraete, 1998). Ultrasonic pretreatment seems to be promising, since full-scale studies have showed an improvement in sludge dewaterability (Khanal *et al.*, 2007).

- Use of additives (Yadvika *et al.*, 2004):
  - The addition of powdered leaves, crop residues, etc. seem to increase the biogas production; the additives create a more favourable environment for the microorganisms and offer sites for the substrate local concentration

through adsorption which seem to have a positive impact on biogas production (Chandra and Gupta, 1997; Dar and Tandon, 1987; Somayaji and Khanna, 1994; Babu *et al.*, 1994).

- The addition of microbial strains (such as cellulolytic bacteria and fungi or cell lysate) increases the substrate digestibility (Tirumale and Nand, 1994; Attar *et al.*, 1998; Geeta *et al.*, 1994; Dohanyos *et al.*, 1997).
- The addition of inorganic elements, adsorbents or chelating agents seems to help through various ways, by: (1) increasing the density of bacterial flocs (Shimizu, 1992), (2) contributing to the formation of vital metalcontaining enzymes (Geeta *et al.*, 1990), (3) solubilising trace elements via combining a chelating agent with a metal (Gaddy, 1994), and (4) increasing stability via adsorption (Patel *et al.*, 1992; Patel and Madamwar, 1994).

### 12.5 Process modelling

Mathematical models have been developed to improve understanding of the complex dynamics of the anaerobic digestion process and to predict the response of the anaerobic systems to changes in operating conditions (hydraulic retention time, organic load, temperature, etc.). Models are tools for process design, control strategies, diagnosis or prediction of system performance under conditions of increasing or decreasing load and variation of feeding characteristics.

There are many types of anaerobic models ranging from steady-state models to single- or double- or multi-step dynamic models. Steady-state models can be applied in systems where the fluctuations in the feed characteristics and organic loading are minimised. This basis of static design modelling has been employed in several text books (Tchobanoglous and Burton, 1991). In most cases, however, the model should provide information about the dynamics of the system towards changes in the input of the system. Dynamic models can be utilised successfully in control schemes or for simulation purposes. Depending on the purpose, the model should be simple enough including only the basic steps for describing the dynamics of the core process (control) or more complex including as many steps as possible making it widely applicable (simulation). Table 12.1 refers to various models developed in the last three decades.

The basis for simplifying a model is the 'rate limiting step' concept, that is, the last slow step in a sequence of reactions that determines the overall rate of a multistep process. The two slowest steps recognised in anaerobic systems are hydrolysis and acetoclastic methanogenesis (Gossett and Belser, 1982; Pavlostathis and Gossett, 1986, 1988). When the feedstock contains particulate organic matter (sludge, organic fraction of municipal solid wastes, solid residues, etc.), the rate of hydrolysis usually determines the overall rate. In this case, the steps that follow are usually considered to be at pseudo steady state and can be described by algebraic equations reducing the degree of complexity of the model. In the absence of particulate matter in the feedstock, acetoclastic methanogenesis is

Hydrolysis	Acidogenesis	Acetogenesis	Methanogenesis	Source
			Volatile fatty acids (acetate) $\rightarrow CH_4$ , $CO_2$	Graef and Andrews (1974)
Particulate organics → soluble organics (glucose)	Soluble organics → volatile fatty acids		Volatile fatty acids (acetate) $\rightarrow CH_4$ , $CO_2$	Hill and Barth (1977)
	Glucose → butyrate, propionate, acetate	Butyrate, propionate → acetate H2, CO2 → acetate	Acetate $\rightarrow CH_4$ H <sub>2</sub> , CO <sub>2</sub> $\rightarrow CH_4$	Hill (1982)
Particulate organics $\rightarrow$ aminoacids, sugars, fatty acids	Aminoacids, sugars, fatty acids → propionate, acetate	Propionate → acetate	Acetate $\rightarrow CH_4$ H <sub>2</sub> , CO <sub>2</sub> $\rightarrow CH_4$	Bryers (1985)
	Glucose → butyrate, propionate, acetate	Butyrate, propionate → acetate	Acetate $\rightarrow$ CH <sub>4</sub> H <sub>2</sub> , CO <sub>2</sub> $\rightarrow$ CH <sub>4</sub>	Mosey (1983) Pullammanappallil <i>et al.</i> (1991)
Particulate organics (fats, carbohydrates, proteins) → soluble organics	Soluble organics → acetate		Acetate $\rightarrow CH_4$	Kleinstreuer and Powegha (1982)
	Soluble organics (glucose) → volatile fatty acids (acetate)		Acetate → CH₄	Moletta <i>et al.</i> (1986)
Easily biodegradable biomass → soluble organics	Soluble organics → volatile fatty acids		Volatile fatty acids $\rightarrow CH_4$	Smith <i>et al.</i> (1988)
	Glucose → lactate, butyrate, propionate, acetate Lactate → propionate, acetate	Butyrate, propionate → acetate	Acetate $\rightarrow CH_4$ H <sub>2</sub> , CO <sub>2</sub> $\rightarrow CH_4$	Costello <i>et al.</i> (1991)
Particulate carbohydrates → soluble carbohydrates	Soluble carbohydrates → butyrate, propionate, acetate	Butyrate, propionate → acetate	Acetate $\rightarrow CH_4$	Angelidaki <i>et al.</i> (1993)
Particulate carbohydrates, proteins, fats → aminoacids, sugars, fatty acids	Aminoacids and sugars → propionate, acetate fatty acids → acetate	Propionate → acetate	Acetate $\rightarrow$ CH <sub>4</sub> H <sub>2</sub> , CO <sub>2</sub> $\rightarrow$ CH <sub>4</sub>	Siegrist <i>et al.</i> (2002)
Particulate carbohydrates, proteins → soluble carbohydrates and proteins	Soluble carbohydrates and proteins, other organics → propionate, acetate	Propionate → acetate	Acetate → CH₄	Gavala <i>et al.</i> (1996)
Particulate organics→carbohydrates, proteins, fats → aminoacids, sugars, fatty acids	Aminoacids and sugars → butyrate, propionate, acetate Fatty acids → acetate	Butyrate, propionate → acetate	Acetate $\rightarrow$ CH <sub>4</sub> H <sub>2</sub> , CO <sub>2</sub> $\rightarrow$ CH <sub>4</sub>	Batstone <i>et al.</i> (2002)

Table 12.1 Steps involved in various models of anaerobic digestion developed in the last three decades

the rate limiting step, considering the preceding steps to be at a pseudo steady state.

On the other hand, in the case of multistep models, the steps usually included are:

- Hydrolysis of particulate matter: Although the mechanisms of the individual hydrolysis steps are known, the hydrolysis step is usually lumped as a single first order process (Eastman and Ferguson, 1981; Pavlostathis and Giraldo-Gomez, 1991).
- Acidogenesis of soluble organic matter: Modelling of sugar fermentation is challenging due to the variety of the possible fermentation products and the determination of the stoichiometry (subjected to the regulation mechanisms prevailed in the heterogeneous group of acidogens). The main pathways acknowledged to take place are towards formation of butyrate, acetate, ethanol and acetate, as well as propionate and acetate as end products (Ren et al., 1997; Batstone et al., 2002). Lactate has been also considered important to be included among the sugar fermentation products (Costello et al., 1991). In mixed fermentation processes, the mechanisms that regulate the composition of the fermentation product mixture have not been elucidated completely and as a result, modelling of this step has not yet been effective (Mosey, 1983; Costello et al., 1991; Ruzicka, 1996). This limitation has become critical due to the increasing interest concerning the production of biohydrogen produced along with the other sugar fermentation metabolic products. As far as the modelling of amino acid fermentation is concerned, the pathways based on Stickland reactions have been proposed (Ramsay and Pullammanappallil, 2001).
- Acetogenesis and methanogensis: Both steps have been extensively and successfully simulated. However, the incorporation of hydrogen, free ammonia and pH effects on the kinetics of both steps can be further improved.

In the biochemical part of the model, the kinetic relationships expressing the bioreaction rates are very important. There is a wide range of kinetics that can be applied in each step of the anaerobic digestion (Pavlostathis and Giraldo-Gomez, 1991), but the most common relationship is the Monod kinetics:

$$\rho = k_{\rm m} \cdot \frac{\rm S}{\rm K_{\rm S} + \rm S} \cdot \rm X$$
[12.1]

where  $\rho$  is the consumption rate of the substrate,  $k_m$  is the maximum specific consumption rate constant,  $K_s$  is the saturation constant, S is the concentration of the substrate and X is the concentration of the microorganisms that consume the substrate.

Equation 12.1 can be extended to include any inhibition or regulation mechanisms if required (Batstone, 2006):

$$\rho = k_{\rm m} \cdot \frac{S}{K_{\rm s} + S} \cdot X \cdot I_1 \cdot I_2 \cdot \dots \cdot I_n$$
[12.2]

where  $I_1, I_2, \ldots, I_n$  are functions expressing inhibition mechanisms can include classic non-competitive or competitive inhibition, or empirical formulas. Modification of Monod kinetics to account for all kinds of product, cell and substrate inhibition has been extensively applied in biochemical engineering (Levenspiel, 1980; Han and Levenspiel, 1988).

Moreover, apart from the biochemical part of the model, it is important to include a physicochemical part to assess the gas transfer and calculate the pH (if required in the biochemical part). The gas transfer can be modelled by applying the gas-liquid transfer theory for each gas. Equilibrium can also be assumed for those gases that are practically insoluble in water, such as hydrogen and methane. The total gas production rate can be calculated as the sum of individual gas production rates. Gas flow can also be derived by setting a pressure difference between the headspace and the atmosphere (Batstone, 2006). pH calculation requires solving algebraic equations derived from the equilibrium of weak acids and bases as well as charge balance. Dissociation of acids and bases can also be considered as dynamic processes evolving at a high rate.

In 2002, a group of scientists expert on anaerobic digestion modelling constructed the anaerobic digestion model (ADM1) to be a frame model basis for several applications in anaerobic digestion (Batstone *et al.*, 2002). The model has been used as a reference basis for many extensions made by several researchers afterwards to utilise it in specific applications, such as, the anaerobic digestion of brewery wastewater in a full scale high rate system (Ramsay and Pullammanappallili, 2005).

Depending on the bioreactor design (homogeneous or heterogeneous system), simple hydraulic or more complex models taking into account mass transfer phenomena can be developed. Mass transfer is important in the case of 'biofilm' bioreactors where microorganisms are attached on the surface of an inert material (anaerobic filters) or attached on each other (UASB). There are different degrees of complexity that can be entailed in modelling biofilm bioreactors. Several parts of the bioreactor can be considered to be homogeneous, as in UASB reactors modelled by Bolle *et al.* (1986), thus a non homogeneous system can be depicted by a combination of the homogeneous systems connected. In a more complex model design, the layers composing the biofilm in a filter or the granule in a UASB are taken into account, with each layer being formed by a specific group of microorganisms. Many UASB models assume that the granules are spherical and the relative concentration of the granules is also assumed to remain constant. Saravanan and Sreekrishnan (2006) review the various model approaches available for biofilm reactors extensively.

### 12.6 Process monitoring and control

Control of anaerobic digestion is crucial in order to secure or even to maximise the performance of the process. In order to develop a control scheme the following steps should be considered:

- Definition of the control objective: The objective could be as simple as the pH stabilisation or more complicated involving stabilisation and optimisation of the bioreactor operation in terms of biogas production or chemical oxygen demand removal. Since optimisation and stabilisation are conflicting objectives, the control law should be sophisticated enough to meet these targets in the best way.
- Selection of the suitable measurements: The properties of a suitable measurement to be used in a control scheme are the ability to reflect the process state and its changes due to disturbances (sensitivity), as well as the time response and the simplicity of the measurement method. The most common measurements in anaerobic digesters (Table 12.2) are:
  - Biogas flow: The biogas production rate and especially the performance in methane is the most commonly used measurement to detect the process stability. A reduction in the biogas production rate usually suggests that the volatile fatty acids have been accumulated as a result of overloading or presence of a toxicant. However, any change in this parameter is caused by process instability and cannot be an early warning, that is, it is not sensitive enough.
  - Biogas composition: The principle gases in the headspace of an anaerobic digester are CO2 and CH4. When CO2 increases relatively in proportion to CH<sub>4</sub>, process imbalance has already evolved and, consequently, this index cannot be used as an early indicator. On the other hand, CO<sub>2</sub> in the gas phase is influenced by changes in alkalinity and pH in the bioreactor, and as a result when pH control is applied in low buffered systems, changes in its value do not reflect process instability (Ryhiner et al., 1992). Another important gas found at very low concentrations is hydrogen. Hydrogen has been suggested as an early reliable measurement for early detection of an imminent imbalance (Archer et al., 1986, Molina et al., 2009). Hydrogen is a significant intermediate compound regulating the performance of the acetogens. Accumulation of hydrogen entails accumulation of volatile fatty acids due to thermodynamic limitations of acetogenesis. It should be kept lower than 40 nM (which corresponds to a partial pressure less than 6 Pa at 35°C). Archer et al., (1986) monitoring hydrogen partial pressure in the headspace predicted an accumulation of volatile fatty acids 3-6 h before it happened. However, the changes in the hydrogen concentration cannot be correlated necessarily with imbalance (Guwy et al., 1997). Measuring hydrogen in the headspace does not correspond to the actual concentration sensed by the microorganisms which are in the aqueous phase. This is why measurement of dissolved hydrogen is suggested as a more reliable index (Pauss et al., 1990; Frigon and Guiot, 1995). Hydrogen sulphide and carbon monoxide can also be detected but they are not important for control purposes.
  - Volatile fatty acids: They are the most important intermediate compounds in anaerobic digestion since their accumulation leads to pH decrease,

stressing the methanogens further. The increase in acetate concentration under overload conditions does not indicate necessarily process imbalance if the biogas production rate has also increased. In this case, the system may operate at a higher acetate concentration at a new steady state, without rejecting the possibility of process failure. However, propionate and butyrate accumulation denote signs of imbalance since it usually happens when hydrogen concentration increases. Propionate is accumulated first, since its conversion requires six times lower concentration of hydrogen than butyrate (Ozturk, 1991). Therefore propionate has been suggested as a suitable indicator for process imbalance (Pullammanappallil *et al.*, 1998; Boe et al., 2008), along with butyrate (Renard et al., 1991), the ratio of propionate to butyrate (Hill, 1982), and the iso forms of butyrate and valerate (Cobb and Hill, 1991; Ahring et al., 1995). Depending on the metabolic pathways prevailing in an anerobic bioreactor, volatile fatty acids may be formed at various concentrations and there cannot be a rule of thumb for a 'safe' level of volatile fatty acids securing stable operation. For example, Pullammanappallil et al., (2001) found that operation of a controlled, glucose fed bioreactor in the presence of phenol remained stable at a high propionate concentration (2750 mg/L). Moreover, the inhibition of volatile fatty acids is pH dependant and their inhibitory effect increases at pH values ranging from 6 to 7.5.

- pH: Monitoring pH is very important since it affects the microorganisms activity and can be correlated with changes in acids and bases as well as anions and cations produced or consumed as a result of the metabolic activity. However, it cannot be used to evaluate the state of the system since it is affected by the buffer capacity of the liquid (determined mostly by the bicarbonate, ammonia, volatile fatty acids).
- Alkalinity: It is distinguished in total and bicarbonate alkalinity. Total alkalinity is measured through titration to pH 3.7 (Powel and Archer, 1989) and expresses the capacity of an anaerobic system to maintain the pH under acidification. However, total alkalinity increases as the volatile fatty acid concentration increases. Therefore, the bicarbonate alkalinity, measured through titration to 5.75, can reflect the effective buffer capacity of the system. Various methods have been developed for the on-line measurement of the bicarbonate alkalinity (Table 12.2).
- Organic matter: Common parameters such as the total and volatile solids, chemical oxygen demand, total organic matter and biochemical methane potential (preferable to biological oxygen demand in the case of anaerobic systems) express the aggregate organic matter present in a digester and, correlated with the organic matter of the influent, give an accurate estimate of the organic matter removal. However, these are time consuming, offline measurements, except from the total organic carbon method which can be applied on-line in the case of anaerobic systems with low

Parameter	Method	Source
Biogas flow	Volumetric displacement	Angelidaki <i>et al.</i> (1992), Veiga <i>et al.</i> (1990), Nilsson <i>et al.</i> (1988), Liu <i>et al.</i> (2004), Walker <i>et al.</i> (2009)
	Manometric	Guwy <i>et al.</i> (1995), James <i>et al.</i> (1990), Soto <i>et al.</i> (1993), Smith and Stöckle (2008)
Methane	Gas chromatography Infrared analyser	
	Treatment of biogas with soda lime	Soto <i>et al.</i> (1993), Sponza (2003), Rozzi and Remigi (2004)
Hydrogen	Mercury-mercuric oxide detector cell	Pauss <i>et al.</i> (1990)
	Exhale hydrogen monitor Palladium metal oxide semiconductors	Collins and Paskins (1987) Pauss <i>et al.</i> (1990)
	Thermistor thermal conductivity	Björnsson (2000), Björnsson <i>et al.</i> (2001), Lundström (1981)
Dissolved hydrogen	Amperometric probe	Kuroda <i>et al.</i> (1991)
	Hydrogen/air fuel cell	Pauss <i>et al.</i> (1990)
	Mass spectrometry	Meyer and Heinzle (1998)
	Silicon or Teflon membrane tubing to transfer dissolved hydrogen to gas phase	Cord-Ruwisch <i>et al.</i> (1997), Björnsson <i>et al.</i> (2001)
Volatile fatty acids	Gas chromatography (off-line)	
	On-line sampling and gas chromatography	Ryhiner <i>et al.</i> (1992), Ryhiner <i>et al.</i> (1993), Zumbusch <i>et al.</i> (1994), Pind <i>et al.</i> (2003)
	Gas phase extraction at $pH < 2$	Boe <i>et al.</i> (2008)
	Indirectly via titration	Powel and Archer (1989), Lahav and Morgan (2004), Molina <i>et al.</i> (2009), Salonen <i>et al.</i> (2009)
Alkalinity	Titration	APHA (2005), Hawkes <i>et al.</i> (1993), Lahav and Morgan (2004), Molina <i>et al.</i> (2009), Salonen <i>et al.</i> (2009)
Total, volatile solids	Drying	APHA (2005)
Chemical oxygen demand	Oxidation and spectrometry	APHA (2005)
Total organic carbon	Infrared analyser	Ryhiner <i>et al.</i> (1993)
Biochemical methane potential	Bioassay	Owen <i>et al.</i> (1979), Owens and Chynoweth (1993)

Table 12.2 Major methods used for monitoring the anaerobic digestion process

solid content (Table 12.2). Therefore, they are not suitable for on-line controllers.

- Metabolic activity: The physicochemical parameters available for measurement respond to changes in the metabolic activity of the anaerobic microorganisms, but the correlation is not always direct. Since the success of a control scheme applied on anaerobic systems is based on directing the microbial activity to the desired performance, its assessment is very important. The microbial activity can be evaluated through measurement of the specific methanogenic activity (Ince et al., 1995; Garcia-Morales et al., 1996; Fountoulakis et al., 2004; Dong et al., 2009; Montero et al., 2009), application of molecular techniques (for the qualitative and quantitative detection of specific microorganisms based on the DNA and RNA probing (Macario and de Macario, 1993; Macario et al., 1989; Raskin et al., 1994; Montero et al., 2009) and detection of changes in cellular components such as enzymes (NADH and coenzyme  $F_{420}$ ) (Perk and Chynoweth, 1991; Amann et al., 1998), ATP (Chung and Neethling, 1988) and phospholipid fatty acids (Nordberg et al., 2000). Moreover measurement of the activity of certain enzymes and application of microcalorimetry (heat released in an anaerobic ecosystem which can be correlated to the size of the microbial population, the metabolic state and activity) have also been used for monitoring (Switzenbaum et al., 1990). Since most of the analytical procedures required for assessing the metabolic activity are elaborate and time consuming or require samples of low solid content, the utilisation of these measurements is limited for on-line control, but can be used off-line to give a better insight of the system status.
- Manipulated variables: The manipulated variables are operating parameters through which the process state can be affected and led to the satisfaction of the control objective according to the applied control law.

The most common manipulated variable is the dilution rate, or equivalently, the hydraulic retention time (inverse of the dilution rate). The dilution rate should generally be lower than the maximum specific growth rate constant of the slowest growing microorganisms group to avoid wash out in a continuously stirred tank reactor. In such type of bioreactor, the sludge (solids) retention time coincides with the hydraulic retention time. In order to increase the conversion rate, recirculation of the sludge is often applied to increase the biomass concentration. In systems fed with waste of high solid content, the liquid effluent stream is recirculated to provide it with nutrients and microorganisms. In both cases, the hydraulic and sludge retention times are separated and can be manipulated independently. The extent of manipulation of the hydraulic retention time is restricted in practice given the waste storage capacity of the treatment plants (a few hours to a few days). The hydraulic retention time in thermophilic conditions can be as low as 4–6 d, while in mesophilic conditions

it is 10–15 d, although higher values of the hydraulic retention time result in more stable operation (Pind *et al.*, 2001).

The organic loading rate, influenced by the organic content of the waste at a given hydraulic retention time, is another manipulated parameter, but since the organic content of the waste does not vary, its use is rather restricted.

In the case of more than one waste stream being commonly digested (codigestion), the composition of the waste mixture is another manipulated variable. In codigestion, wastes can be combined to make up for nutrient deficiencies, dilute the inhibitory compounds of waste stream, enhance the process yield of low potential waste (Angelidaki and Ahring 1997; Gavala *et al.*, 1999; Angelidaki and Ellegaard 2003; Alatriste-Mondragon *et al.*, 2006; Nielsen and Angelidaki 2008; Dareioti *et al.*, 2009; Li *et al.*, 2009; Shanmugam and Horan, 2009).

Other manipulated variables are the acid, base or bicarbonate addition rates to control the pH or alkalinity in the bioreactor or the feed (Pind *et al.*, 2001). pH and alkalinity control require the addition of chemicals, which raise the cost of the process. An alternative is to recycle the  $CO_2$  produced in order to increase the alkalinity, but this is not effective in case the bioreactor pH is lower than 6.5 (Romli *et al.*, 1994).

• The control law: It is the information flow structure through which the manipulated variables are handled based on the measurements. The complexity of the control law is determined by the diversity of the control objective. As a result, the controller can be simple (on-off, proportional, proportional-integrated-differential), more complicated adaptive model-based, empirical (expert systems), fuzzy or neural network-based. Detailed references on the various control systems having applied on anaerobic digesters can be found in Pind *et al.* (2003), Liu (2003) and Boe (2006).

# 12.7 Biogas utilisation

Biogas consists primarily of methane and carbon dioxide, but also smaller amounts of hydrogen sulphide, ammonia and traces of hydrogen, nitrogen, carbon monoxide, saturated or halogenated carbohydrates and oxygen may be present. The biogas is usually saturated with water vapour and may also contain particles and siloxanes. The energy content is determined by the methane content (1 kWh per m<sup>3</sup> of biogas with 10% of methane).

The biogas can be used in as many applications as the natural gas (heating, combined heat and power systems, fuel cells). There may be different specifications for biogas to be used in different applications, especially, when biogas is to be used in stationary appliances or to be fed to a pipeline grid. The biogas needs purification to improve its quality in most cases.

Hydrogen sulphide and its oxidation products are the major 'contaminants' of the biogas (corrosive) with a maximum permitted concentration of 5 ppm.

Hydrogen sulphide reacts with most metals. Conditions of high pressure and temperature (prevailing during storage or usage of biogas) favour the reactivity of this contaminant. Sulphur dioxide also lowers the dew point (temperature to which a given volume of gas must be cooled, at constant barometric pressure, for water vapour to condense into water) in the stack gas. There are biological methods for hydrogen sulphide removal that can be applied in the anaerobic digester as well as other physicochemical methods applicable after biogas has been collected. The biological methods include the supply of small air amounts to activate the sulphide oxidising microorganisms (Thiobacillus) grown in a micro-aerophilic environment on  $CO_2$  (autotrophic). The hydrogen sulphide is converted to elemental sulphur but also to sulphate. A combination of biological filter (containing sulphide oxidising microorganisms) and a water scrubbing step can be used alternatively. Physicochemical methods include usage of iron containing compounds (iron chloride, iron oxide), activated carbon, water scrubbing, dimethylether of polyethylene glycol (or selexol) scrubbing and NaOH scrubbing. Iron chloride can be supplied into the digester which forms iron sulphide (insoluble) and is applied when hydrogen sulphide is produced at high concentrations.

Humidity should also be removed because the presence of water favours the formation of sulphur oxidation products. Water is condensed and frozen under conditions of high pressure during biogas storage.

Carbon dioxide must also be removed if the biogas has to meet the natural gas specifications. Especially if biogas has to be used a vehicle fuel, it must be enriched in methane. Suitable methods for carbon dioxide removal include water absorption, polyethylene glycol absorption (the carbon dioxide is better dissolved in selexol), carbon molecular sieves (a series of carbon columns is used to save energy required for pressure application) and membrane separation (with gas phase in both sides of the membrane – high pressure or with a liquid phase in the one side for absorption of the carbon dioxide while diffusing through the membrane – low pressure). Halogenated compounds (present in landfill biogas) and oxygen (due to air entrance when landfill biogas is collected) must be removed too. The requirements for removal of these constituents are reported in Table 12.3 depending on the biogas usage.

# 12.8 Existing biogas installations

There are biogas plants worldwide with different degree of technical development. The overall world market was approximately two billion euro in 2006 and is expected to increase to more than 25 billion by 2020 total (http://www.hkc22. com/biogas.html, updated in July 2008). Measures are taken worldwide to promote biogas and its market development (Sakulin, 2009). Among the initiatives taken, the feed-in tariff is a motivation to promote the adoption of renewable energy policy through legislation. According to this, the regional or national

Application	H <sub>2</sub> S	CO <sub>2</sub>	H <sub>2</sub> O
Gas heater (boiler)	<1000 ppm	No	No
Kitchen stove	Yes	No	No
Combined heat and power device	<1000 ppm	No	No condensation
Vehicle fuel	Yes	Recommended	Yes
Natural gas grid	Yes	Yes	Yes

*Table 12.3* Removal of biogas components based on the usage

Source: IEA, Bioenergy – biogas upgrade and utilisation, Task 24: Energy from biological conversion of organic waste.

Country	Farm biogas plants	Annual biogas production (m <sup>3</sup> 10 <sup>6</sup> )	Installed electricity capacity (MW)	Installed electricity capacity per plant (kW)	Maximum feed-in tariff (€/kWh)
Austria	119	67.94	14.84	124.71	0.165
Belgium	5	56.13	12.26	533.04	0.124
Czech Republic	10	5.23	1.14	114.16	0.074
Denmark	40	387.61	84.67	1365.59	0.106
France	5	213.49	31.39	373.72	0.215
Germany	1900	1144.53	250.00	131.58	
Greece	1	70.59	11.96	797.58	
Ireland	13	9.29	2.02	155.54	
Italy	67	282.21	61.64	856.16	0.130
Lithuania	4	11.50	2.51	627.85	
Netherlands	15				0.068
Poland	15				
Portugal	100				0.060
Sweden	6				
Switzerland	69				0.100
UK	60	462.39	101.00	623.46	

Table 12.4 Statistics on biogas plants in Europe

Source: http://www.adnett.org/, last updates: 6 April 2005.

electricity utilities are obliged to buy electricity generated from renewable sources (solar power, wind power, hydropower, geothermal as well as biomass). Table 12.4 lists the feed-in tariff for several European countries.

Europe has high-tech biogas plants in operation, with Germany being the leader. In 2006, 900 plants were built, reaching 3600 in total (Helmut Kaiser) in Germany. A market size of 7.5 billion euro, 30% export and 85000 jobs are expected by 2020 in Germany. As in Germany, Denmark also has a variety of biogas plants of different capacity. The digestion of manure and organic waste is

a well-established practice in Denmark with 20 centralised plants and over 35 on-farm plants (Raven and Gregersen, 2007), although there is a decline in the construction of new plants. In Austria and Switzerland, there are mostly small farm scale plants due to the national agricultural structure. In Sweden, there are also quite a few large scale plants (Fischer and Krieg, 2001). Table 12.4 reports the status of biogas plants and capacity in Europe.

Unlike Europe, experience with anaerobic digestion in North America is quite limited. Farm-based anaerobic digestion in North America only began out of necessity for odour control due to urban encroachment (Lusk, 1998). In the USA, which rejected the Kyoto protocol, most of the methane from wastes is allowed to escape into the atmosphere where it contributes to global warming. However, there is a strong movement towards the use of renewable energy from biogas. The development of anaerobic digesters for livestock manure stabilisation and energy production has accelerated at a very fast pace over the past few years. According to the EPA, about 111 digesters operate at livestock facilities in USA up to 2007 (U.S. EPA, 2007). The energy production was 215 million KWh (electrical energy: 170 million KWh). It was estimated that besides electricity generation, the biogas was used in boilers and fed in the natural gas gridding (after upgrade) or flared for odour control. In Canada, approximately 16 farm-scale anaerobic digesters operate or are being built (Wohlgemut, 2006). In 2006, the Ontario government implemented a Renewable Energy Standard Offer Program, which guaranteed farmers a higher rate for biogas-produced electricity, along with a financial assistance programme designed to reduce the capital costs of digester construction (Hilborn et al., 2007). On the other hand, in the Manitoba province, anaerobic digestion is less promoted due to the well-established and cost-effective hydroelectricity industry (Wohlgemut, 2006).

In Australia, the installed capacity for biogas was 458 MW in 2001. Electricity generation from biogas has increased considerably from 23 GWh in 1995 to 729 GWh in 2001, an average growth rate of 78% per year. Wastes from food processing plants, livestock manure and human sewage are the primary feedstocks for biogas production. Most of the installed capacity is at sewage treatment plants, which are considered highly cost effective.

In developing or less developed areas of the world, anaerobic digestion is spreading fast. In Asia (mostly China and India, but also Vietnam, Thailand, etc.) there are millions of low-tech, hand-made, plants consisting of underground, non-insulated digesters in operation for decades (Fischer and Krieg, 2001). Manure and food residues are the main feedstocks used and the biogas energy generated is used for cooking and lighting. According to the ministry of agriculture in China, 15 million households in China were using biogas in 2004, with the aim to increasing this number to 27 million by 2010, which will account for over 10% of all rural households. By the end of 2005 there were 2492 medium and large-scale biogas digesters in livestock and poultry farms, while 137 000 biogas bioreactors had been constructed for the household wastewater treatment (van Nes, 2006). In

order to support the development of renewable energy sources, China enforces suitable legislation and takes steps to promote industrialisation of the construction of biogas plants. In India, 3.67 million biogas units were installed in 2004. The ministry of non-conventional energy resources implements a programme (national biogas and manure management programme) for providing financial, training and technical support for the construction and maintenance of biogas plants. Similar initiatives have been taken in Nepal and Vietnam (van Nes, 2006). European companies and organisations, mainly from Germany, Denmark and Austria, have already entered the Japanese and Korean market and transferred high-tech anaerobic technology, while they promote anaerobic digestion to the developing countries such as China, India, etc.

In Africa, there are attempts by international organisations and foreign aid agencies to promote biogas technology. Some digesters have been installed in some sub-Saharan countries, making use of feedstocks such as slaughterhouse wastes, municipal wastes, industrial waste, animal dung and human excreta. Small-scale biogas plants have been established all over the continent (Table 12.5) but only few of them are operational (Parawira, 2009). Insufficient know-how concerning anaerobic technology is claimed to be the main reason for

Country	Number of small/ medium (100 m <sup>3</sup> )	Number of large digesters (>100 m <sup>3</sup> )
Botswana	Several	1
Burkina Faso	>30	—
Burundi	>279	—
Egypt	Several	Few
Ethiopia	Several	>1
Ghana	Several	_
Côte D'Ivoire	Several	1
Kenya	>500	_
Lesotho	40	—
Malawi	_	1
Morocco	Several	_
Nigeria	Few	—
Rwanda	Several	Few/Several
Sudan	Several	_
South Africa	Several	Several
Swaziland	Several	—
Tanzania	>1000	—
Tunisia	>40	_
Uganda	Few	—
Zambia	Few	_
Zimbabwe	>100	_

	Table	12.5	Biogas	units	in	Africa
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Source: Parawira (2009).

inadequate operational potential of the installed plants. In some cases, the installation of the plant is of poor quality and the appropriate maintenance lacks.

In Latin America, many biogas plants operate in the agricultural, industrial and municipal sectors. Biogas is mainly used for cooking, lighting, as town gas or as vehicle fuel. The quantity of biogas produced in Latin America was estimated at 217 million m<sup>3</sup> per year in 1993 (Ni *et al.*, 1993).

The future of biogas as a competitive biofuel relies on the economic feasibility of the anaerobic technology. The income sources of a biogas plant are the energy and fertiliser sales as well as the tipping fees for receiving off-farm waste. Remuneration or subsidies from the government is an extra income. If the cost of energy production is too high, the biogas can be flared to eliminate odours and greenhouse gas emissions, but this is not a viable option. The costs of biogas production are distinguished into the capital (or investment) and operational costs for the installation of the plant and its maintenance, respectively. Capital costs are determined mainly by the size of the plant and the technology selected. The price of components (feeders, stirrers, CHP, etc.) and construction materials (concrete, steel) also affect the investment cost. The operational costs include maintenance of the biogas plant, labour costs, insurance and other utilities. Laaber *et al.* (2007) estimated that the capital costs vary between 3000 and 5000  $\notin/kW_{electricity}$  for the anaerobic digestion of energy crops, while the operational costs range between 2 and 4.5 ct/kWh<sub>electricity</sub>.

### 12.9 Conclusions and future trends

Anaerobic digestion is a well established, reliable and successful technology implemented worldwide. In the past years, anaerobic systems required high capital costs and elaborate expertise to operate and maintain with low process efficiencies. However, in the last decade, deployment of successful operating systems increased the technical reliability of anaerobic digesters reducing the requirements for maintenance and special operative skills. Moreover, many national and regional programmes have been designed to cost-share in the development of anaerobic systems and promote the energy policies expanding the renewable energy markets. The EU policy has set a goal of supplying 20% of the European energy demands from renewable energy sources by 2020. The major sources for conversion to gaseous, liquid and solid biofuels will be from farming and forestry. At least 25% of the total bioenergy may come from biogas produced from wet organic materials such as animal manure, crop silages, wet organic food and feed residues, etc. (Holm-Nielsen et al., 2007). There is also a growing interest in the anaerobic digestion of the organic fraction of the municipal solid waste on an attempt to reduce the materials flow to landfills. Apart from the biogas production benefits, anaerobic digestion offers opportunities for enhanced recycling of organics and nutrients. Codigestion of organically derived municipal waste with sewage sludge, manure and a range of food processing and other

industrial organic wastes is also promising as it may result in producing more nutrient balanced fertilisers.

A significant category of lignocellulosic feedstock (primarily crops residues) has also been considered to be exploited through anaerobic digestion schemes. There are several pretreatment methods developed that would allow the enhancement of the rate-limiting hydrolysis for the solubilisation of the particulate substrates. Due to the expensive pretreatment technologies, it seems more feasible and, therefore, promising to focus on the post treatment of the residue streams obtained after anaerobic digestion, in order to take advantage of the nutrients or other high added value materials contained. That is, anaerobic digestion of lignocellulosic feedstocks could be more effective if incorporated in biorefinery concepts.

Practices promoting the biogas technology may also include dissemination of know-how to all countries worldwide, as well as further research and development on (1) small scale systems (to go from the economy of scale to the economy of numbers), (2) process optimisation through efficient process control that would strike a balance between the often conflicting targets of biogas maximisation and waste stabilisation, (3) pretreatment for enhancing the process performance on lignocellulosic biomass, (4) post-treatment (for further valorisation of all by-products and reduction of the transportation costs), (5) molecular and microbiological level that would give a better insight of the process, (6) reduction of capital and management costs, and (7) more effective elimination of odours to minimise negative social impacts.

# 12.10 Sources of further information and advice

The European Anaerobic Digestion Network: http://www.adnett.org/index.html The AgSTAR Program: http://www.epa.gov/agstar/index.html

Renewable Energy, Purdue University: http://www.ces.purdue.edu/bioenergy Unit of Bioconversion of Crops and Wastes: http://www.emu-bioconversion.eu/ The AD Community: An Independent Web Site: http://www.anaerobic-digestion

.com/index.php

Superflex/tools/supergas: http://www.superflex.net/tools/supergas/technology.shtml ISKA Percolation Company: http://www.iska-gmbh.de/en/index.php

BTA-Technologies: http://bta-international.de/

ArrowBio: http://arrowbio.com/

Kompogas: http://www.kompogas.com

Entec Biogas GmbH: http://www.entec-biogas.at/en/index.html

England's Official Information Portal on Anaerobic Digestion: http://www .biogas-info.co.uk/

Small-Scale Biogas Use with Biogidesters in Rural Costa Rica: http://www .ruralcostarica.com/biodigester.html

What Is a Biogas Plant?: http://www.wisegeek.com/what-is-a-biogas-plant.htm

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# G. ANTONOPOULOU, I. NTAIKOU, K. STAMATELATOU and G. LYBERATOS, University of Patras, Greece

**Abstract:** This chapter discusses all the biological hydrogen production processes such as indirect and direct water biophotolysis, biological water gas shift, photo and dark fermentation and hydrogen production through microbial electrolysis cells. Dark fermentation or fermentative hydrogen production is focused on this chapter, since it is considered as the most promising compared to all biological hydrogen production methods. However, there are significant remaining barriers to practical application. The chapter includes the limitations of each process and suggests several methods that are aimed at overcoming these barriers.

**Key words:** biohydrogen, biological hydrogen production processes, fermentative hydrogen production, advantages and limitations.

### 13.1 Hydrogen

Hydrogen is a colorless, odorless gas that accounts for 75% of the universe mass. It is also the simplest element in the periodic table, since its atom consists of only one proton and one electron. Despite its simplicity and abundance, hydrogen does not exist naturally as a gas, but is found in water, biomass and fossil fuels (gasoline and natural gas), where it is always combined with chemical bonds with other elements such as oxygen, carbon and nitrogen. In order to get hydrogen into a useful form, it must be extracted and separated from these substances. These 'extraction' processes are often quite energy intensive. For this reason, many efforts have been invested on the exploration and development of cost-effective and efficient methods of hydrogen production.

Apart from being a very useful reagent for the production of many chemicals, hydrogen is also the most clean and environmentally friendly fuel, which produces water instead of greenhouse gases when burned and possesses a high energy yield of 122 kJ/g, which is 2.75 times greater than that of hydrocarbon fuels. Hydrogen is indeed considered a viable alternative fuel and the 'energy carrier' of the future.

Today, hydrogen finds a wide range of industrial applications being a widely used feedstock for the production of chemicals, hydrogenation of fats and oils in food industry, production of electronic devices, processing steel and also for desulfurization and re-formulation of gasoline in refineries. Furthermore it is used in NASA's space programme as fuel for the space shuttles and in fuel cells for heat and electricity generation. Proton exchange membrane fuel cells (PEMFC) fed with hydrogen are



13.1 Distribution station of hydrogen in Tsurumi of Japan (Iwasaki, 2003).

believed to be the best type of fuel cell that could be used as power sources in vehicles and have the potential to replace the gasoline and diesel in internal combustion engines (http://www.fctec.com). Beyond its use in fuel cells, hydrogen could be directly burned in a fossil internal combustion engine (very similar to petrol or gas-fired engines) to produce mechanical energy without producing  $CO_2$  at the point of use. According to the National Hydrogen Program of the United States, the contribution of hydrogen to the total energy market is projected to be 8–10% by 2025 (Armor, 1999). In Fig. 13.1, a hydrogen station in Tsurumi of Japan is depicted.

### 13.2 Biological hydrogen production methods

There exist various hydrogen production methods using fossil fuels, biomass or water as feedstocks. In this chapter, we focus on biological hydrogen production processes. These processes have the advantage that they can take place at ambient temperature and atmospheric pressure. The main obstacles are the lower rates and yields of hydrogen produced, compared to the thermo-chemical or electro-chemical processes. During the last 30 years, a great number of studies dealing with biological hydrogen production have been published, but up to now, only little progress on practical applications has been achieved.

Biological hydrogen production can occur through bacteria and algae. It is based on the fact that all biological related processes are controlled by hydrogen producing enzymes, such as hydrogenase and nitrogenase which catalyse the simplest chemical reaction:

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \leftrightarrow \mathrm{H}_{2}$$

$$[13.1]$$

These processes can be classified into the following categories while their main characteristics are summarized in Table 13.1 (Levin *et al.*, 2004; Call and Logan, 2008) and are described in the sequel: in the following sections.

# 13.2.1 Biophotolysis of water using algae and cyanobacteria

Under certain conditions, green algae and cyanobacteria can use water-splitting photosynthetic processes to generate molecular hydrogen. Biophotolysis-based hydrogen production can be carried out via direct or indirect means as identified by whether or not light is irradiated during hydrogen evolution (Benemann, 1998). A brief description of the principles, the systems (Fig. 13.2) and the main bottlenecks for the practical application of both processes are given below.



13.2 Direct (a) and indirect (b) biophotolysis of water.

<i>Table 13.1</i> Biolo	ogical hydrogen productic	on technologi	es		
Process	Microorganisms	Feedstock	Advantages	Disadvantages	H <sub>2</sub> synthesis rate mmol H <sub>2</sub> /L/h
Direct biophotolysis	Green algae Chlamydomonas	Water, sunlight	H <sub>2</sub> production directly from water and sunlight	High intensity of light	0.07
	reinhardtii		Solar conversion energy increased by tenfold as compared to trees, crops	O <sub>2</sub> can be dangerous for the system Lower photochemical efficiency	
Indirect biophotolysis	Cyanobacteria Anabaena variabilis	Water, sunlight	H <sub>2</sub> production from water	Removal of uptake hydrogenase enzymes because of H <sub>2</sub> degradation	0.355
			Ability to fix N <sub>2</sub> from atmosphere	30% O <sub>2</sub> present in gas mixture Sunlight requirement	
Photo- fermentation	Photosynthetic bacteria Rhodobacter spheroides	Biomass, sunlight	A wide spectral light energy can be used	Inhibitory effect of $O_2$ on nitrogenase	0.16
			Different organic wastes as substrates	Low light conversion efficiency	
Biological water gas shift	Photo-heterotrophic bacteria	CO	Low temperatures and pressures	Demand of CO source	96
	Rhodospirillum rubrum Rubrivivax gelatinosus		High conversion efficiency	Inhibitory effect of $O_2$	
Dark fermentation	Fermentative bacteria Enterobacter aerogenes	Biomass	H <sub>2</sub> production all day, without light independence	Low obtained H <sub>2</sub> yields	8.2–121
	Clostridium butyricum Mixed microbial cultures		Variety of carbon sources as substrates	$\mathrm{O}_2$ is a strong inhibitor of hydrogenase	
			Valuable metabolites, as byproducts	$\mathrm{CO}_2$ present in the gas	
			No O <sub>2</sub> limitation	Requirement of further treatment of the fermentation effluent, before disposal	
Microbial Electrolysis Cells	Electrode reducing microorganisms	Biomass, electricity	Higher yields No use of O <sub>2</sub>	Electricity supply Competitive methane generation	5.8
	deubacter, Shewahella sps				

#### Direct biophotolysis

Direct biophotolysis is an attractive process since solar energy is used to convert a readily available substrate, the water, to oxygen and hydrogen, according to the reaction:

$$2H_2O \xrightarrow{\text{solar energy}} 2H_2 + O_2$$
 [13.2]

In this process, electrons are generated from water through photosynthesis and then transferred via an electron carrier – ferredoxin (Fd), to hydrogen producing enzyme – hydrogenase, to produce hydrogen. Microalgae, such as green algae and Cyanobacteria (blue-green algae), containing hydrogenases, have the ability to produce hydrogen. Well-known cyanobacteria that have been found to produce hydrogen in lab scale bioreactors are *Anabaena* sp. such as *Anabaena cylindrical* (Weissman and Benemann, 1977), *Anabaena variabilis* (Sveshnikov *et al.*, 1997; Borodin *et al.*, 2000) and *Synechococcus* (Howarth and Codd, 1985). *Chlamydomonas reinhardtii* is the representative of green microalgae for biohydrogen production (Tsygankov *et al.*, 2006; Griesbeck *et al.*, 2006; White and Melis, 2006). Other algal species such as *Chlorococcum littorale* and *Platymonas subcordiformis* have also been investigated for hydrogen production (Schnackenberg *et al.*, 1996; Guan *et al.*, 2004).

The main drawback of direct biophotolysis is that the process is limited because of the strong inhibition of hydrogenase by the oxygen produced. Thus, for the sustainability of hydrogen production, it is necessary to maintain the oxygen content at a low level, below 0.1% (Hallenbeck and Benemann, 2002). In practice, it is very difficult to maintain such low partial pressures of oxygen, without additional energy and cost demands. For example, neutral gases such as helium could be sparged in the reactor, in order to eliminate oxygen, but the supplemental cost of helium and hydrogen dilution, makes this solution unacceptable. Another approach involves the addition of oxygen absorbers (Hallenbeck and Benemann, 2002) but now this seems not practical at larger scale.

Other limitations, such as the low light conversion efficiencies and the requirement for large photobioreactors, make the process impractical for largescale application as it becomes inefficient from an economical point of view. It ought to be mentioned that a number of approaches to improve  $H_2$  production by green algae are currently under investigation. These include genetic engineering of light gathering antennae (Polle *et al.*, 2002), optimization of light input into photobioreactors (Gordon, 2002) and improvements to the two-phase  $H_2$ production systems used with green algae (Laurinavichene *et al.*, 2002a; Tsygankov *et al.*, 2002). Another challenge is the modelling and simulation of photolytic systems to support systems design and optimization.

#### Indirect biophotolysis

Hydrogen production by cyanobacteria and microalge through photosynthesis can be represented by the following reactions:

$$6H_2O + 6CO_2 \xrightarrow{\text{Solar energy}} C_6H_{12}O_6 + 6O_2$$
 [13.3]

$$6H_2O + C_6H_{12}O_6 \xrightarrow{\text{Solar energy}} 12H_2 + 6CO_2 \qquad [13.4]$$

In indirect biophotolysis, the electrons are derived from water by photoautotrophic cells. As presented in reactions [13.3] and [13.4], the process consists of two stages in series: the first one is photosynthesis for carbohydrate accumulation and the second one, is dark fermentation of the endogenous carbohydrates for hydrogen production. In this way, the oxygen and hydrogen evolutions may be temporally and/or spatially separated (Benemann, 1996). This separation not only avoids the incompatibility of oxygen and hydrogen evolution (e.g. enzyme deactivation and the explosive property of the gas mixture), which are key barriers to direct biophotolysis, but also makes hydrogen purification relatively easy, because  $CO_2$  can be conveniently removed from the generated H<sub>2</sub>/CO<sub>2</sub> mixture (Belafi-Bako *et al.*, 2006).

Cyanobacteria have attracted more research interest for hydrogen production via indirect biophotolysis than microalgae. Such cyanobacteria species include *Anabaena* sp., *Spirulina* sp., marine cyanobacteria such as *Calothrix* sp., *Synechococcus* sp. and *Geobacter* sp. *Anabaena cylindrical* is a well-known hydrogen producing cyanobacterium, but *Anabaena variabilis* has received more attention in the recent years, because of higher hydrogen yields compared to the other species (Masukawa *et al.*, 2001). Emphasis has been given to increase the activity of hydrogen producing enzymes and to develop mutants of *Anabaena* sp. to increase the rate of hydrogen production. However, at the present time, the hydrogen production rate by *Anabaena* sp. is considerably lower than that obtained by dark or photofermentations which are described below (Pinto *et al.*, 2002; Liu *et al.*, 2006a).

Nowadays, indirect biophotolysis, just like direct biophotolysis, is an immature technology, applied only at laboratory scale. It should be noted that indirect water photolysis, is under active research and development, since several factors are still crucial for further improvement in technology. Environmental conditions, such as light, temperature, salinity, nutrient availability and gas atmosphere (the presence of oxygen, nitrogen or methane) play an important role in the hydrogen production efficiency (Dutta *et al.*, 2005). In addition, in order to improve hydrogen production rates and yields using cyanobacteria, methods such as screening of wild-type strains possessing highly active hydrogen evolving enzymes (nitogenases and/or hydrogenases) (Pinto *et al.*, 2002), or genetic modification of strains to increase the hydrogenase activity, are under investigation. Finally, optimization of cultivation conditions such as light intensity, pH, temperature, and nutrient content, will contribute to increased H<sub>2</sub> production.

#### Systems for hydrogen production via water biophotolysis

Several types of bioreactors have been used for hydrogen production via water biophotolysis (direct and indirect). These reactors require adequate entry of light, which could be sunlight or another artificial light, such as red light. To maximize the area of incident light, which allows high cell growth and hydrogen production, the reactor design should provide a high surface-to-volume ratio. In addition, it should allow sterilization and easy handling. Furthermore, the photobioreactor should be an enclosed system so that the produced hydrogen could be collected without any losses. Photobioreactors can be mainly divided into three types: vertical column reactor, tubular type and flat panel photobioreactor. A summary of bioreactor types and their properties is provided in Table 13.2 (Dutta *et al.*, 2005).

### 13.2.2 Hydrogen production via biological water gas shift

Biological water gas shift reaction is a new concept for hydrogen production. Certain photo-heterotrophic bacteria such as *Rhodospirillum rubrum* and *Rubrivivax gelatinosus* can perform this reaction at ambient temperature and pressure. These bacteria can survive in the dark using CO as the sole carbon source, oxidizing it to  $CO_2$  and reducing H<sup>+</sup> to H<sub>2</sub>, according to the reaction:

$$CO + H_2O \Leftrightarrow CO_2 + H_2, \quad \Delta G^0 = -20,1 \text{ kJ/mol}$$
 [13.5]

Bioreactor type	Species used	Advantage	Disadvantage
Vertical Column	Spirulina platensi	• Simple and cost- effective design	• Lack of control on light
		<ul> <li>Greater rate of mass transfer</li> </ul>	<ul> <li>Wide fluctuations in productivity</li> </ul>
Flat panel	Spirulina platensi	<ul> <li>Greater control of incident light</li> </ul>	<ul> <li>Cost for production is high</li> </ul>
		Effective control of gas     pressure	<ul> <li>Complicated design and more maintenance</li> </ul>
Tubular	Arthrospira platensis,	<ul> <li>Flexibility in volume-to- surface-area ratio</li> </ul>	• Poor mass transfer
	Anabaena variabilis PK84, Anabaena variabilis	<ul> <li>Flexibility in shifting the place receiving light</li> </ul>	
	ATCC 29413 Anabaena variabilis PK84	<ul> <li>Gives higher biomass with internal static mixture</li> </ul>	

Table 13.2 Different bioreactor types used for water biophotolysis (Dutta et al., 2005)

The thermodynamics of this reaction are very favorable to CO-oxidation and  $H_2$  synthesis, since the equilibrium of this reaction lies strongly to the right. The purple non-sulfur bacteria perform CO–water gas shift reaction in darkness, converting 100% of CO into a near-stoichiometric amount of hydrogen and also assimilate CO into new cell mass in the light, when CO is the sole source of carbon (Maness and Weaver, 1997). They are also able to utilize CO in the presence of other organic substrates.

The need to reduce residual CO to very low levels makes the mass transport of gaseous CO into an aqueous bacterial suspension the rate limiting step in the process and is the main challenge for bioreactor design. This suggests the need for counter-current gas-liquid contacting systems, as in trickling filters used in waste treatment or plug-flow systems typical in commercial gas biofiltration processes (Andrews and Noah, 1995).

However, hydrogen production through biological water–gas shift reaction is still at laboratory scale and thus, intensive research, including scale-up, should be done in order to become an applicable technology. Genetic strain improvements and identification of suitable microorganisms that have high CO uptake ability are strategies that should further increase the obtained hydrogen rates and yields. Process economics are presently uncertain since they depend on the required size of the bioreactors and the losses inherent in such ambient pressure–temperature conversion process. Wolfrum *et al.* (2003) have conducted a detailed study to compare the biological water–gas shift reaction with the conventional water–gas shift process is lower due to the elimination of the need for a reformer and the expensive equipment required for the thermochemical process. Thus, the microbial water–gas shift reaction may be a good candidate for near-term biohydrogen process development. Indeed, some authors consider this process as the most promising for commercial application.

### 13.2.3 Hydrogen production via microbial electrolysis cells

Hydrogen can also be produced through a microbial electrolysis cells (MEC) which is a modified microbial fuel cell (MFC) converting directly biodegradable material into hydrogen instead of electricity (Call and Logan, 2008). In a typical MFC, protons released by the oxidation of the organic substrate in the anode, migrate through an external load to the cathode to combine with oxygen and form water. A MEC operates under anaerobic conditions (no oxygen in the cathode) and a small external voltage is applied to the cell, so that protons and electrons produced by the anodic reaction are combined at the cathode to form hydrogen. The power supply is required since hydrogen generation from the protons and the electrons is thermodynamically unfavorable (Liu *et al.*, 2005) and with external potential application, the cathode potential increases overcoming the thermodynamic barrier. The required external potential for a MEC is theoretically 110 mV. In practice, the minimum applied voltage

to produce hydrogen from the bioelectrolysis of a pure substrate such as acetate, has been found to be more than 250 mV due to ohmic resistances and electrode overpotentials. This value is still much lower than the respective one required for direct electrolysis of water, which is 1210 mV (Liu *et al.*, 2005).

MEC can potentially produce about 8–9 mol  $H_2/mol$  of glucose consumed, which is double, compared to the typical 4 mol  $H_2/mol$  glucose, achieved in a conventional fermentation process (see Section 13.3.2). The MEC compared to the MFC, has the advantage that there is no need for oxygen in the cathodic chamber affecting in the better performance of the system (Das and Veziroglu, 2008) and leading to improved efficiencies from an economic point of view.

Under certain conditions, methane which is competitive to hydrogen can also be generated in a MFC. Strategies to control and suppress methanogenesis have been proposed (Call and Logan, 2008), resulting in more complex and expensive systems, with significantly increased operation requirements. Up to now, the majority of researchers on MECs systems have investigated the use of pure compounds (primarily acetate) as the substrate. However, alternative substrates such as domestic or animal wastewaters can be used (Ditzig *et al.*, 2007; Wagner *et al.*, 2009) but the performance of such systems is limited in terms of hydrogen yields due to the appreciable methane gas production.

Different reactor configurations have been proposed for hydrogen production through MECs. Two-chamber (Liu et al., 2005; Cheng and Logan, 2007) or one-chamber (Call and Logan, 2008) systems, with membrane (Rozendal et al., 2007) or without membrane (Call and Logan, 2008) are some of the characteristics of the MECs developed in laboratories. One of the challenges in scaling up MECs is the cost of the cathode and the cathode catalysts since most MECs use platinum applied on carbon cloth (Ditzig et al., 2007; Call and Logan, 2008) or carbon paper (Liu et al., 2008). In order to improve the performance and economic feasibility of MECs, platinum needs to be replaced by alternative low-cost cathode materials such as stainless steel (Selembo et al., 2009) or microbial biocathodes (Jeremiasse *et al.*, in press). In addition to these limitations, securing viable continuous operation, operation under carbon limited conditions, ways of increasing the microorganisms tolerance to impurities, and the possible use of alternative feedstocks, are all issues that need to be investigated. Although promising, this is still an experimental method for hydrogen production which has not been evolved beyond the laboratory since certain microbiological, technological and economic challenges need to be resolved before full-scale implementation.

# 13.2.4 Photoheterotrophic or photo-fermentative hydrogen production

Photoheterotrophic or photo-fermentative hydrogen production refers to the microbial process, during which organic substrates are oxidized under anaerobic

conditions in the presence of light, generating hydrogen and carbon dioxide. Photo-fermentative hydrogen production is generally carried out by prokaryotic microorganisms called purple non-sulfur bacteria (PNS) (Basak and Das, 2007), although lately the process has also been reported to be carried out by eukaryotic microorganisms, that is, green algae (Hemschemeier and Happe, 2005). Photosynthetic microorganisms convert light energy into chemical energy in the form of chemical bonds, via the pathway of photosynthesis.

Contrary to dark fermentation (see Section 13.3), in which the enzyme hydrogenase catalyses hydrogen production, nitrogenase is the key enzyme for the photo-fermentative process of PNS. Under nitrogen-deficient conditions, nitrogenases can also catalyse the generation of molecular hydrogen using light energy and reduced compounds (such as organic acids) as the electron donors, where ferredoxin acts as the electron carrier (Das and Veziroglu, 2001). Light as an energy source is necessary for such reactions to take place, since their Gibbs energy is positive and thus they are not thermodynamically favored:

$$CH_{3}COOH + 2H_{2}O + "hv" \rightarrow 2CO_{2} + 4H_{2} \quad \Delta G^{o} = +75.2 \text{ kJ/mol} \quad [13.6]$$

As shown in Table 13.3, in most photo-fermentative biohydrogen studies pure cultures of the genera *Rhodopseudomonas*, *Rhodobacter* and *Rhodospirillum* have been used, whereas studies with other genera such as *Rubrivivax* (Li and Fang, 2008) and *Rhodobium* (Kawaguchi *et al.*, 2001), as well as with mixed cultures (Zhang *et al.*, 2002; Fang *et al.*, 2005) have also been reported. Malate and glutamate were commonly selected as carbon and nitrogen sources, respectively. However, the use of other carbon sources such as the acids lactic, succinic, acetic, propionic and butyric, or their salts, has also been investigated for their potential to be converted into hydrogen either in the form of synthetic substrates or as parts of actual waste streams.

In order to evaluate the performance of a photo-fermentative hydrogen production system, the efficiency with which light energy is converted to energy in the form of hydrogen, the so-called photochemical efficiency (PE) or light conversion efficiency, has to be taken into consideration (Akkerman *et al.*, 2002). It thus becomes obvious that the efficient utilization of light energy, provided either by a physical (sunlight) or an artificial source, is of extreme importance for the construction of a feasible energy production system (Miyake and Kawamura, 1987). Factors affecting PE include wavelength and intensity of light, cell concentration in the culture, surface to volume ratio of the culture (reactor geometry) and light penetration in the reactor. It is widely accepted that optimal light utilization is indispensable for maximal hydrogen production.

As shown in Table 13.3, in most studies one or more artificial light sources have been selected among florescent lamps, halogen lamps, optical fibers, neon tubes, light-emitting diodes and photosynthetically active radiations (PARs), which however could become a hindrance to the overall economic viability of a full-scale application. Sunlight on the other hand, is a free and abundant light source, which

Microorganism	Substrate	Reactor operation/ configuration	Nitrogen source	Condition of microorganisms	Light source/l <sub>energy</sub>	Reference
Rhodopseudomonas palustris	Malic acid, acetic acid	Fed-batch/ cylindrical glass	Glutamic acid	Suspended	Lamps light source from one and two	Carlozzi and Lambardi, 2007
	Palm oil mill effluent (POME)	Batch/serum bottles	No addition, TKN ∞60 mg l⁻¹	Suspended	bulbs/2–5 klux	Jamil <i>et al.</i> , 2009
	Glycerol	Batch/serum bottles	Glutamate, 2–6 mM	Suspended	Panel of 50 W halogen spotlights/-	Sabourin- Provost and Hallenbeck, 2009
			Ammonium, 0–4 mM			
	Glucose	Continuous/flat, polymethyl methacrylate	Ammonium	Immobilized in (PVA)-boric acid gel	LED mounted on the topside/3–11 klux	Tian <i>et al.</i> , 2009
Rhodopseudomonas faecalis	Sodium Acetate	Fed-batch/serum bottles	Sodium glutamate, 10 mM	Suspended	60 W incandescent lamps/4 klux	Ren <i>et al.</i> , 2009a
	Glucose	Batch/serum bottles	Sodium glutamate, 1 g I <sup>-1</sup>	Immobilized in agar gel	60 W incandescent lamps/4 klux	Ding <i>et al.</i> , 2009
	Sodium acetate	Batch/serum bottles	Glutamate, 10 mM	Suspended	60 W incandescent lamps/4 klux	Ren <i>et al.</i> , 2009b
Rhodobacter capsulatus	Acidified <i>Miscanthus</i> hydrolysate, acetate, lactate, fructose	Batch, sealed glass bottles	Sodium glutamate, 2 mM	Suspended	150 W halogen lamp/1,370 µmol photons/m²/s	Uyar <i>et al.</i> , 2009
	Lactate	Batch/flat glass	Sodium alutamate, 7 mM	Suspended	Sodium-vapour lamp 600 W/	Obeid <i>et al.</i> , 2009
	Malate	Batch	Sodium glutamate, 2 mM	Suspended	lamps/4 klux	Öztürk <i>et al.,</i> 2006 (Continued)

Microorganism	Substrate	Reactor operation/ configuration	Nitrogen source	Condition of microorganisms	Light source/l <sub>energy</sub>	Reference
Rhodobacter sphaeroides	DL- malate	Batch/triple jacketed vertical, cylindrical, glass	Glutamate, 2 mM	Suspended	Tungsten filament lamp placed in central axis of reactor/15± 1.1 W m <sup>-2</sup>	Basak and Das, 2009
	Mixed substrate of acetate, butyrate, ethanol	Batch/water jacket glass column	Sodium glutamate, 10 mM	Suspended	100 W lamps 5.5±0.5 klux	Nath <i>et al.</i> , 2008
	Raw, acidified or clay pretreated olive mill wastewater	Batch/glass vessels	No addition	Suspended	150 W tungsten lamp/4 klux	Eroglu <i>et al.,</i> 2006
	Succinate	Batch	Ammonium chloride 0.04 w/v	Suspended	Lamps/2.4 klux	Chalam <i>et al.,</i> 1996
Rhodospirillum rubrum	Sodium succinate	Batch	Glutamate 3 mM	Suspended	Fluorescent and incandescent light bulbs/60 W m <sup>-2</sup>	Melnicki <i>et al.,</i> 2008
	Acidified cassava wastewater	Batch/serum bottles	Glutamic acid, ammonium nitrate	Suspended	Fluorescence lamp/6000 candela/m²	Reungsang <i>et al.</i> , 2007
	Mixed substrate of acetate, malate	Batch/cylindrical, glass	L-glutamate 23 mM	Immobilized in agar gel	Lamps/20 klux	Planchard <i>et al.,</i> 1989
	Lactate, cheese whey	Continuous, HRT 74 h rectangular	L-glutamate 15 mM	Suspended	100-W spot-light tungsten	Zurrer and Bachofen, 1979

Table 13.3 Continued

can be used for direct irradiation of the bioreactor or amplified by the use of solarenergy-excited optical fibers (Chen *et al.*, 2008a). A drawback of using sunlight could be the periodicity of the light source; an obstacle that could be surpassed by the addition of solar-energy-excited optical fibers, accompanied by light-dependent resistors, which can ensure the stability of light energy (Chen *et al.*, 2008a).

In order to develop commercially viable processes, the influence of many other factors has to be taken into consideration. The nitrogen source is one of the most critical parameters for effective photo-fermentative hydrogen production. An organic nitrogen source, such as glutamic acid or inorganic salts or more complex organic nitrogen sources such as veast extract, seems to be necessary for efficient hydrogen production regardless of the species of microorganism used. The effect of the type and concentration of the carbon source used as substrate (Carlozzi and Lambardi, 2009), the C/N and C/N/P ratios (Reungsang et al., 2007) as well as the physicochemical conditions of growth such as pH (Tian et al., 2009) and temperature (He et al., 2006) have been widely studied and optimized, since they seem to have a severe effect on both the final hydrogen yield and the hydrogen production rate. Regarding pH, the optimum value is reported to be 7 in most cases, whereas the optimum temperature is reported to be 30°C. A general conclusion from all these studies is that the photo-fermentation processes seem to be favored by a high ratio of C/N, irradiation with light of saturating intensity, under anaerobic conditions with optimal temperature and pH, depending on the specific microorganism used.

There are three major types of photo-bioreactors developed for hydrogen production that is tubular, flat panel and bubble column reactors. The features of these photo-bioreactors have been reviewed by Akkerman et al. (2002) and the importance of PE in hydrogen production was strongly emphasized. The main advantage of tubular and column photo-bioreactors is that their geometry allows for quite efficient mixing of the culture, and thus the exposure of the microbial cell to light is more equally distributed. The way to scale-up is to connect a number of tubes via manifolds. Flat panel reactors consist of a rectangular transparent box with a depth of only 1-5 cm. The height and width can be varied to some extent, but in practice only panels with a height and width both smaller than 1 m have been studied. The advantage of these systems is the large surface that can be illuminated either using sunlight or artificial means. The main disadvantage of such type of reactors is the high consumption of energy used for maintaining efficient air supply and mixing of the liquid. Many scaled-up versions of photo-bioreactors consist of repeating many of the smaller photo-bioreactor units, with its practical implications.

Finally, the quantitative description of photo-fermentative hydrogen production seems to be quite complex, due to the large number of parameters that have to be taken into account. Simple models such as the Luedeking–Piret model (Basak and Das, 2009), the logistic model (He *et al.*, 2009), the Monod equations (Obeid *et al.*, 2009) and the Gompertz equation (Nath *et al.*, 2008) have been used in order to fit

experimental results regarding biomass growth and cumulative hydrogen generation, but so far very few studies have dealt with the development of complex structured kinetic models, properly incorporating specialized for photo-fermentative hydrogen production parameters such as light intensity and wavelength influence. A simple kinetic model for photo-fermentative biohydrogen production has been developed by Gadhamshetty *et al.* (2008) for batch bioreactors, where it was assumed that sufficient light intensity and optimal C/N ratio were available under stressful nitrogen concentrations. The proposed model used *Rhodobacter sphaeroides* as the model biomass and contained 17 parameters to describe cell growth, substrate consumption, and hydrogen evolution as well as inhibition of the process by biomass, light intensity, and substrate. Based on sensitivity analysis performed with the validated model, only 6 of the 17 parameters were found to be significant and it was indicated that the range of optimal light intensity for maximum hydrogen yield from malate by *R. sphaeroides* was 150–250 W/m<sup>2</sup>.

### 13.2.5 Hydrogen production via dark fermentation

Dark fermentation is an alternative method for biological hydrogen production from biomass. It is a process which is carried out in the dark, under anaerobic conditions, and it is directly related to the acidogenic stage of anaerobic digestion process. It has been considered as a viable and effective method, since it is carried out at ambient temperatures and pressures, without photoenergy, so that the cost of hydrogen production is estimated as 340 times lower than that of the photosynthetic processes (Morimoto, 2002). The hydrogen-producing enzymes (hydrogenases) can be utilized in dark fermentations by using pure microbial cultures or by a mixture of anaerobic microorganisms. Since no oxygen is produced or consumed in these reactions, hydrogenase is less likely to be inactivated by oxygen. Organic wastes from agriculture or sewage can be fed into large anaerobic bioreactors, achieving the dual goals of waste management and hydrogen production. Dark fermentation as a method of hydrogen production does not have the demand of expensive photo-bioreactors, which are necessary for direct biophotolysis and photo-fermentation. Fermentative hydrogen production is focused on this handbook, since it is considered as the most promising compared to all biological hydrogen production methods. Brief comparison of biomass materials that can be used for biohydrogen production, microorganisms available, factors limiting biohydrogen production, modelling and process optimization and lastly strategies for process improvement will be highlighted in the next chapter section.

## 13.3 Fermentative hydrogen production

### 13.3.1 Feedstocks for fermentative hydrogen production

It is well founded that carbohydrates are the main source of hydrogen during fermentative processes and therefore wastes/wastewater or agricultural residues,

rich in carbohydrates, can be considered as potential hydrogen feedstocks (Kapdan and Kargi, 2006). The main criteria for substrate selection are: availability, cost, carbohydrate content and biodegradability. Glucose, sucrose and to a lesser extent starch and cellulose are the fermentation substrates mostly studied in the laboratory (Mizuno *et al.*, 2000; Ueno *et al.*, 2001; Fang *et al.*, 2004). They have been used as model substrates for research purposes due to their easy biodegradability and because they can be present in different carbohydrate-rich wastewaters and agricultural wastes. However, synthetic carbohydrates are expensive raw materials for a pilot or full-scale hydrogen production process and therefore the use of zero-cost, rich in carbohydrates wastes, seems to be ideal in real hydrogen production applications.

Rice, winery, noodle, sugar, and molasses manufacturing, olive pulp and cheese whey are among actual wastewaters that have been studied for hydrogen production at a laboratory scale (Table 13.4). In addition, hydrogen could be produced using as feedstocks complex solid wastes, such as wastes from kitchen, food processing, mixed wastes, and municipal wastes containing along with carbohydrates, proteins and fats. In the later case, the hydrogen conversion efficiencies are low, due to the complex structure of the wastes. In general the hydrogen yield from wastes rich in carbohydrates is higher than those rich in proteins and fats.

Moreover, the rich in sugars energy crops, sugar beet, sugar cane and sweet sorghum, as well as the rich in starch energy grains, corn and wheat are among the most suitable substrates for hydrogen production (Table 13.5). However, the potential to produce hydrogen from the residues remaining after harvesting and processing of these starch or sugar crops, that cannot be further exploited in the food industry chain, is more likely to yield a solution with far better overall prospects for economic and environmental sustainability (Lynd et al., 2005). Hydrogen generated from such feedstocks can be characterized as 'secondgeneration hydrogen' since its production is not competitive to food production, but rather a side product of the food production industry. The agricultural residues contain carbohydrate polymers such as cellulose, hemicellulose and lignin, and thus a pre-treatment process (mechanical, chemical or enzymatic) is always necessary, for solubilization of cellulose and hemicellulose to simple sugars, which could easily be degraded by hydrogen-producing bacteria. Rice and wheat straws, corn stover, wheat bran are some of the lignocellulosic feedstocks used for hydrogen generation (Table 13.5). Figure 13.3 presents different potential feedstocks for hydrogen production.

# 13.3.2 Microorganisms for hydrogen production and reactions

Fermentation reactions can be carried out at mesophilic (25–40°C), thermophilic (40–65°C), extreme thermophilic (65–80°C), or hyperthermophilic (>80°C)

			-		
Type of waste/ wastewater	Microorganisms	Operation mode	H <sub>2</sub> production rate	Maximum H <sub>2</sub> yield	References
Rice winery wastewater	Mixed culture	Continuous	9.33 L/gVSS/d 3.81 L/L/d	2.14 mol/mol hexose	Yu <i>et al.</i> , 2002
Sugar factory wastewater	Mixed thermophilic culture	Continuous	4.4 L/L/d	2.6 mol/mol hexose	Ueno <i>et al.</i> , 1996
Potato processing wastewater	Mixed mesophilic culture	Batch		2.8 L/L wastewater	Van Ginkel <i>et al.</i> , 2005
Olive pulp	Mixed mesophilic culture	Continuous	0.26 L/L/d	0.19 mole/kg TS	Koutrouli <i>et al.</i> , 2009
Cheese whey	Mixed mesophilic indigenous microbial culture	Continuous	2.51 L/L/d	0.9 mol/mol hexose	Antonopoulou <i>et al.</i> , 2008a
Dairy wastewater	Mixed mesophilic culture	Continuous	1.59 mmol H <sub>2</sub> /L/d		Venkata Mohan <i>et al.</i> , 2007
Molasses	Mixed mesophilic culture	Continuous	4.8 L/L/d		Ren <i>et al.</i> , 2007
Food waste – sewage sludge	Mixed mesophilic culture	Batch	2.67 L/gVSS/d	122.9 mL/g COD carbohydrate	Kim <i>et al.</i> , 2004
Food waste	Mixed thermophilic culture	Batch	0.28 8 L/gVSS/d	1.8 mol/mol hexose	Shin <i>et al.</i> , 2004
OFMSW	Mixed mesophilic culture	Batch	0.4 L/g VSS/d	0.15 L/g OFMSW	Lay <i>et al.</i> , 1999

Table 13.4 Actual wastes/wastewaters used for fermentative hydrogen production

OFMSW: organic fraction of municipal solid wastes

Table 13.5 Exploitation	of rich in carbohydrates crops	or their residue	es for fermentativ	e hydrogen production	
Crops/residues	Microorganisms	Operation mode	H <sub>2</sub> production rate	Maximum H <sub>2</sub> yield	References
Corn starch	Mixed mesophilic cultures	Continuous	2.57 L/L/d	0.51 mol/mol hexose added	Arooj <i>et al.</i> , 2008
Wheat starch	Mixed mesophilic cultures	Continuous		1.26 mol/mol hexose	Hussy <i>et al.</i> , 2003
Sweet sorghum extract	Indigenous microbial mesophilic culture	Continuous	8.52 L/L/d	0.86 mol/mol hexose	Antonopoulou <i>et al.,</i> 2008b
Sweet sorghum extract	Rumicococcus albus	Batch		2.61 mol/mol hexose	Ntaikou <i>et al.</i> , 2008
Sweet sorghum residues	Rumicococcus albus	Batch		2.59 mol/mol hexose	Ntaikou <i>et al.</i> , 2008
Wheat straw	Caldicellulosiruptor saccharolyticus	Batch		3.8 mol/mol glucose (44.7 L/kg dry biomass)	lvanova <i>et al.</i> , 2009
Maize leaves Pretreatment: enzymatic hydrolysis	Caldicellulosiruptor saccharolyticus	Batch		3.6 mol/mol glucose (81.5 L/kg dry biomass	lvanova <i>et al.</i> , 2009
Corn stalks Pretreatment: acid hydrolysis	Mixed mesophilic cultures	Batch	0.1824 L/d	0.150 L/kg TVS	Zhang <i>et al.</i> , 2007a
Corn stover Pretreatment: acid hydrolysis	Thermoanaerobacterium thermosaccharolyticum W16	Batch	3.305 L/d	2.24 mol/mol hexose	Cao <i>et al.</i> , 2009
Sugarcane bagasse hydrolysate Pretreatment: acid hydrolysis	Clostridium butyricum	Batch	1.611 L/L/d	1.73 mol/mol total sugar	Pattra <i>et al.</i> , 2008

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*13.3* Different potential feedstocks for hydrogen production from biomass.

temperatures. Hydrogen production could be achieved either by using pure cultures of hydrogen producing bacteria grown in the dark on carbohydrate-rich substrates or by mixed acidogenic microbial cultures, selected by natural environments such as soil, wastewater sludge, and compost. At a full-scale application, a mixed culture system would be cheaper to operate, easier to control, and would have a broader choice of feedstocks (Valdez-Vazquez *et al.*, 2005). In Tables 13.4 and 13.5 the different feedstocks used by pure or mixed microbial cultures in lab – scale experiments are presented, since data from full scale applications are not available so far.

Hydrogen production is a specific mechanism to dispose of excess electrons through the activity of the enzyme hydrogenase in bacteria. Bacteria that possess such capability include strict anaerobes (*Clostridia*, methylotrophs, rumen bacteria, methanogenic bacteria, archaea), facultative anaerobes (*Escherichia coli, Enterobacter, Citrobacter*), and even aerobes (*Alcaligenes, Bacillus*). Figure 13.4 presents the morphology of fermentative bacteria selected from a hydrogen producing reactor, at pH 5.5. Among the hydrogen-producing bacteria, *Clostridium* sp. and *Enterobacter*, are the most widely studied. Species of genus *Clostridium* such as *C. butyricum* (Chong *et al.*, 2009), *C. acetobutyricum* (Lin *et al.*, 2007), *C. beijerinckii* (Lin *et al.*, 2007), *C. thermolacticum* (Collet *et al.*, 2004), *C. tyrobutyricum* (Jo *et al.*, 2008), *C. thermocellum* (Levin *et al.*, 2006) and *C. paraputrificum* (Evvyernie *et al.*, 2000) are examples of strict anaerobic and spore-forming microorganisms, generating hydrogen gas during the exponential



*13.4* Morphologies of hydrogen-producing bacteria at pH 5.5 (Fang and Liu, 2002).

growth phase. In parallel, facultative anaerobes such as the species of genus *E. coli* and its modified strains (Manish *et al.*, 2007) and the species of genus *Enterobacter*, such as *E. aerogenes* (Tanisho and Ishiwata, 1994; Yokoi *et al.*, 2001) and *E. cloacae* (Kumar and Das, 2001) have also been used for hydrogen production. In recent years, extensive research has also been carried out in hydrogen production at high temperature, using thermophilic or hyperthermophilic bacteria, since the increase of temperature favours the reaction kinetics. The thermophiles include *Caldicellulosiruptor saccharolyticus* (van Niel *et al.*, 2002), *Thermoanaerobacterium* sp. such as *T. thermosaccharolyticum* (O-Thong *et al.*, 2008) and *Thermotoga* sp. such as *Thermotoga maritima* (Schroder *et al.*, 1994) and *Thermotoga elfii* (de Vrije *et al.*, 2002).

Degradation of glucose (or its isomer hexoses or its polymers, starch, glycogen and cellulose) by mixed microbial culture, under anaerobic conditions is accompanied by the production of hydrogen and various metabolic products, mainly volatile fatty acids ((VFAs) acetic, propionic, and butyric acid), lactic acid, and alcohols (butanol and ethanol), depending on the microbial species present and the prevailing conditions. The hydrogen yield can be correlated stoichiometrically with the final metabolic products, through the reactions describing the individual processes of acidogenesis:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$
[13.7]

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$$
[13.8]

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$$
[13.9]

For complex substrates, the hydrogen production could also be expressed in terms of hydrogen productivity (HP) which is defined as the percentage of influent substrate electrons which are distributed to hydrogen gas (gaseous and dissolved phases) (Kraemer and Bagley, 2005). It is obvious that the production of acetic and butyric acids favors the simultaneous production of hydrogen, with the fermentation of glucose to acetic acid giving the highest theoretical yield of 4 mol of H<sub>2</sub>/mol of glucose (HP = 33%) (reaction [13.7]) and the conversion to butyric acid resulting in 2 mol of H<sub>2</sub>/mol of glucose (HP = 17%) (reaction [13.8]), while the production of propionic acid consumes hydrogen (reaction [13.9]).

From the reactions [13.7], [13.8] and [13.9], it is obvious that the metabolism should be shifted towards acetate and/or butyrate production in order to achieve a high hydrogen yield. *Clostridia sp.* produce a mixture of acids, with butyrate in excess of acetate, upon biological degradation of glucose (Mizuno *et al.*, 2000; Fang and Liu, 2002). In practice, the production of more metabolic products (lactate or ethanol), accompanied by a negative or zero hydrogen yield, results in lower overall yields of hydrogen (HP: 10–20%). Moreover, the metabolism towards acetate may occur via different, non-hydrogen-yielding pathways. In mixed fermentation processes, the microorganisms may select different pathways while converting sugars, as a response to changes in their environment (pH, sugar concentration, etc.). The absence or presence of hydrogen-consuming microorganisms in the microbial consortium also affects the microbial metabolic balance and consequently, the fermentation end products.

In order to harness hydrogen from a fermentative hydrogen production process, the mixed cultures need to be pre-treated in order to suppress as much hydrogenconsuming bacterial activity as possible, while still preserving the activity of the hydrogen-producing bacteria. The pre-treatment method is achieved mostly by relying on the spore-forming characteristics of the hydrogen-producing Clostridium, which is ubiquitous in anaerobic sludge and sediment (Brock et al., 1994). Treating an anaerobic sludge under harsh conditions, Clostridium would have a better chance to survive than the non-spore-forming bacteria, many of which are hydrogen consumers (Lay, 2001). Effective pre-treatment processes include heating (100°C, 15 minutes), acidic (pH = 3, adjusted with ortho-phosphoric acid, 24 hours) or basic treatment, aeration, chemicals addition (chloroform, acetylene), and application of an electric current (3–4.5 V). Another approach involves the use of the indigenous mixed microbial culture already contained in a wastewater through its activation for one day at mesophilic temperatures, a practice that has been applied and proposed by Antonopoulou et al. (2008a; 2008b). The most widely used pre-treatment method for enriching hydrogen - producing bacteria from

mixed microbial inocula is heat – pre-treatment, which combines the simplicity with the effectiveness, securing that *Clostridium* sp. will survive.

# 13.3.3 Key factors affecting fermentative hydrogen production

Apart from the type of microbial inoculum and feedstock, which is used for fermentative hydrogen production, many other factors such as pH, temperature, hydraulic retention time (HRT), nutrients concentration, hydrogen partial pressure, the presence of inhibitors and hydrogen-consuming microorganisms and the reactor configuration, influence the process. Although the role of each parameter in fermentative hydrogen production is well defined, the optimum conditions of a given factor are not clear, so far. For example, it is well known that the pH influences the activities of hydrogen producing microorganisms, since it directly affects the hydrogenase activity (Dabrock *et al.*, 1992) as well as the metabolic pathway followed. However, there is a wide range of pH values, which have been proposed as optimum for fermentative hydrogen production from different feedstocks. The pH range of 5–7.5 (Fang *et al.*, 2002a; Calli *et al.*, 2008) is usually reported as optimum, even though lower or higher pH values such as pH of 4.5 (Ren *et al.*, 1997) and 9.0 (Lee *et al.*, 2002) have also been proposed that are supposed to give the maximum hydrogen yield.

The operational temperature is another important factor affecting the metabolic pathways involved and influencing the whole process. Up to now, most studies on hydrogen production have been carried out under mesophilic conditions, even though it is well known that hydrogen fermentation at high temperatures (thermophilic conditions) has higher hydrogen yield than the mesophilic equivalent, owing to higher suppression of hydrogen-consuming bacteria. Nevertheless, mesophilic biohydrogen production is preferred for preventing the need for external heating, improving the economics of the process.

Regarding the HRT, for pure substrates such as glucose and sucrose, the widely used values are in the range of 3–8 hours, with the lowest being 1 hour (Chang *et al.*, 2002) and the highest 13.7 hours (Fang and Liu, 2004), while for more complex substrates such as starch, an HRT of 15 or 17 hours is suggested to be necessary due to the slow initial step of hydrolysis (Hussy *et al.*, 2003; Lay, 2000).

From this discussion, it becomes clear that the optimum value for each aforementioned key factor depends on the feedstock, the inoculum used and the prevailing conditions under which the experiments are carried out. Thus, predictions of the reactor performance in terms of hydrogen yields and rates as well as carbohydrate conversion efficiency under different conditions are not accurate. So, the selection of the operational conditions of a real scale hydrogen-producing bioreactor at this stage may be safely predicted only on the basis of lab-scale and pilot-scale experiments.

### 13.3.4 Bioreactors used for fermentative hydrogen production

As it has already been mentioned, reactor configuration is considered to be crucial for the overall performance of fermentative hydrogen production process. It is presumed that it influences the reactor's microenvironment, microbial population, hydrodynamic behavior, substrate-consortia contact, etc. (Venkata, 2009). In general, reactors for fermentative hydrogen production can operate in either batch or continuous mode. Batch mode fermentative hydrogen production has been shown to be more suitable for research purposes (Chen *et al.*, 2002; Lee *et al.*, 2002), but any industrially feasible process would most likely have to be performed on a continuous or at least semi-continuous (fed or sequencing batch) basis.

CSTR, is the most commonly used continuous reactor system, offering simple construction, ease of operation and effective homogenous mixing as well as temperature and pH control. In a conventional CSTR, biomass is well suspended in the mixed liquor, which has the same composition as the effluent. However, in this type of reactor, biomass has also the same retention time (SRT) as the HRT, and thus, its concentration in the mixed liquor as well as the hydrogen production is limited, since high dilution rates might cause biomass washout. However, it was recently found that hydrogen-producing biomass in a CSTR could be self-granulated or flocculated under proper conditions (Fang *et al.*, 2002b; Zhang *et al.*, 2004). Another approach to increase the biomass concentration in a CSTR is to immobilize biomass in biofilms or artificial granules made of various support materials such as cuprammonium rayon (Kim, 2002), polyvinyl alcohol (Kim *et al.*, 2003, 2005), polyacrylamide and anionic silica sol (Kim *et al.*, 2003, 2005).

Another category of continuous flow reactors are the systems characterized by physical retention of the microbial biomass, which offer several advantages compared to the conventional CSTR systems. In these systems, the SRT is independent of HRT due to physical retention of the microbial biomass inside the reactor, allowing high cell concentrations and thus high hydrogen volumetric production rates with relatively small reactor volumes. Physical retention of microbial biomass could be accomplished by several different means, including the use of naturally forming flocs or granules of self-immobilized microbes, microbial immobilization on inert materials, microbial-based biofilms or retentive membranes (Hallenbeck and Ghosh, 2009). However, a potential problem with these types of reactors is the loss of hydrogen through the formation of methane due to extended retention of the biomass inside the reactor, permitting the establishment of slow-growing methanogenic populations. Different types of reactor used for continuous hydrogen production, are presented in Table 13.6. Up to now, a comparative study of reactor performance in terms of hydrogen productivity could not be done, since the operational parameters along with reactor configuration, in all these studies, are different.

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Type of reactor	Microorganisms	Feedstock	H <sub>2</sub> production rate	Maximum H <sub>2</sub> yield	References
Continuous stirred tank reactor (CSTR)	Mixed culture	Glucose	0.54 L/L/d	1.7 mol/mol glucose	Lin and Chang, 1999
Upflow anaerobic sludge blanket reactor (UASB)	Sludge from wastewater treatment plant	Sucrose	6.67 L/L/d	1.5 mol/mol sucrose	Chang and Lin, 2004
Packed bed reactor (PBR)	Anaerobic sludge	Sucrose	5.35 L/L/d	0.7 mol/mol sucrose	Li <i>et al.</i> , 2006
Anaerobic sequencing batch reactor (ASBR)	Sludge from wastewater treatment plant	Glucose	5.52 L/L/d	73.8 mL/gCOD	Cheong <i>et al.</i> , 2007
Fixed bed bioreactor with activated carbon (FBBAC)	Sludge from wastewater treatment plan	Sucrose	31.68 L/L/d		Chang <i>et al.</i> , 2002
Anaerobic fluidized bed reactor (AFBR)	Activated sludge and digested sludge	Glucose	29.04 L/L/d	1.8 mol/mol glucose	Zhang <i>et al.</i> , 2007b
Polymethylmethacrylate (PMMA) immobilized cells	Anaerobic sludge	Sucrose	43.2 L/L/d	2.25 mol/mol sucrose	Wu and Chang, 2007
Carrier-induced granular sludge bed (CIGSB)	Sludge from wastewater treatment plant	Sucrose	223.4 L/L/d	4.02 mol/mol	Lee <i>et al.</i> , 2006
Fluidized bed reactor (FBR)	Sludge from wastewater treatment plant	Sucrose	31.72 L/L/d		Wu <i>et al.</i> , 2007
Membrane bioreactor (MBR)	Municipal sewage sludge	Sucrose	40.08 L/L/d	1.51 mol/mol hexose	Lee <i>et al.</i> , 2007
Rhomboidal	Enterobacter cloacae IIT-BT 08	Sucrose	1.855 mol/L/d		Kumar and Das, 2001

Table 13.6 Different reactor systems used for fermentative hydrogen production

### 13.3.5 Purification of hydrogen produced

While direct and indirect photolysis systems produce pure hydrogen, dark-fermentation and photo-fermentation processes, produce a mixed-biogascontaining primarily hydrogen and carbon dioxide (CO<sub>2</sub>), but which may also contain lesser amounts of methane (CH<sub>4</sub>), carbon monoxide (CO) and/or hydrogen sulphide (H<sub>2</sub>S) or ammonia (NH<sub>3</sub>). Moreover, the hydrogen content in the gas phase is in general lower than 50%. PEMFCs require hydrogen at a high purity (>99%) and cannot tolerate CO at concentrations higher than 10 ppm. In order to remove diluting (CO<sub>2</sub>, CH<sub>4</sub>) and/or contaminating (CO) gases, purification of the biogas is essential. Up to now, membrane technologies based on palladium have been proposed as hydrogen purifier in industrial scale applications (Shu *et al.*, 1991).

### 13.3.6 Techniques for improvement of fermentative hydrogen production

At present, development of a practical and efficient hydrogen generation process is a growing concern among the research community. In the last decade, several methods such as mutagenesis, genetic modification or metabolic pathway control have been shown to improve hydrogen yield in laboratory scale experiments. These methods are based on the metabolic pathway and the enzymes which are involved during the fermentative hydrogen production process. Hydrogen evolution follows the NADH (Nicotinamide Adenine Dinucleotide) pathway described by the reaction [13.10] which is catalyzed by the enzyme of hydrogenase. Increased hydrogen yields could be achieved by shifting the chemical reaction so as to increase the amount of NADH usable for hydrogen production:

$$NADH + H^+ \rightarrow NAD^+ + H_2$$
[13.10]

NADH is usually generated by the catabolism of glucose to pyruvate via glycolysis. In general, the yield of hydrogen produced upon mixed acid fermentation of carbohydrates is quite lower than the maximum theoretical yields since sugars fermentation, in addition to VFAs, also leads to the formation of various reduced end-products, such as ethanol, butanol and lactate. These compounds contain additional hydrogen atoms that are not liberated as gas. Therefore, in order to maximize the yield of hydrogen, bacterial metabolism should be directed away from alcohols and reduced acids and towards VFAs production. The conversion of pyruvate to ethanol, butanediol, and lactic acid involves oxidation of NADH. The concentration of NADH would increase if the formation of these alcoholic and acidic metabolites could be blocked (Das and Veziroglu, 2001). Kumar *et al.* (2001) reported enhanced hydrogen yields by blocking the pathways of organic acid formation using the proton-suicide technique with NaBr and NaBrO<sub>3</sub>. A similar enhancement of hydrogen yield using

*E. aerogenes* HU-101 was reported by blocking the formation of alcoholic and acidic metabolites by both allyl alcohol and the proton-suicide technique (Mahyudin *et al.*, 1997).

Operation conditions such as pH, HRT, temperature and hydrogen partial pressure are reported to have a significant effect on metabolic balance. *C. acetobutyricum* has the ability to produce solvents at pH values lower than 5 and under phosphate and iron limiting conditions. In order to obtain high hydrogen yields using *C. acetobutyricum*, a pH above 5, phosphate and iron concentrations above the limiting levels and glucose concentration below 12.5% are recommended (Dabrock *et al.*, 1992). In addition, *clostridia* produce VFAs and hydrogen in the exponential growth phase and rapid alcohol production occurs in late growth phase (Lay, 2000). In order to shift the metabolic pathway towards VFAs production and away from solventogenesis, an application of a low HRT should be essential.

It is also reported that a hydrogen partial pressure higher than 60–100 Pa inhibits the hydrogen production process and in order to obtain maximum hydrogen yields, the hydrogen produced should be removed from the reactor system. For this reason many approaches have been proposed. Mizuno *et al.* (2000) showed that gas sparging with nitrogen enhanced hydrogen yield, while Voolapalli and Stuckey (1998) developed an applicable technique based on a submerged silicone-membrane dissolved gas extraction system, removing hydrogen and carbon dioxide from the reactor volume. Another potentially efficient method for removing hydrogen from the gas stream based on a heated palladium-silver membrane reactor has been proposed by Nielsen *et al.* (2001).

Another strategy for enhancement of hydrogen production by existing pathways can be sought by increasing the flux through gene knockouts of competing pathways or increased homologous expression of enzymes involved in the hydrogen-generating pathways. Up to now, the majority of attempts in laboratories employ the metabolic engineering of *E. coli*, because its genome can be easily manipulated, its metabolism is the best understood of all bacteria and it readily degrades a variety of sugars. For example, Yoshida *et al.* (2005) performed genetic recombination of *E. coli* in conjunction with process manipulation to elevate the efficiency of hydrogen production in the resultant strain SR13. The genetic modification resulted in 2.8-fold increase in hydrogen productivity of SR13 compared with the wild type strain. However, it is still unclear what pathways function under what environmental conditions and what the substrate specificities of all hydrogenase-coupled pathways are involved in *E. coli* (Laurinavichene *et al.*, 2002b).

Metabolic engineering of other native hydrogen-producing microorganisms has so far been limited because there is poor knowledge regarding the existing pathways involved in hydrogen-production system (Jones, 2008). Despite this fact, there are few recent noteworthy examples of improvement in fermentationbased hydrogen production by either genetic or chemical engineering strategies of mesophilic hydrogen producing strains. For example, mutants of both *E. aerogenes* and *E. cloacae* have been isolated after subjecting wild-type strains to chemically selective media, requiring alterations in fermentation product metabolism for survival. In each case, this has resulted in substantial increases in the yield of hydrogen per glucose consumed (Kumar *et al.*, 2001; Ito *et al.*, 2004). In addition, overexpression of a native ferredoxin-dependent hydrogenase in *Clostridium paraputrificum* also resulted in a near doubling of fermentative hydrogen yield (Morimoto *et al.*, 2005). However, progress in the field of metabolic pathway engineering needs to be made in order to develop optimized microorganisms producing high yields of hydrogen, at competitive rates and being able to utilize broader substrate ranges. In this respect, lab-scale hydrogen production will be soon scaled up and applied in real systems converting rich in carbohydrates feedstocks to hydrogen.

### 13.3.7 Hybrid two-stage systems

Even with the improvements noted above, hydrogen yields of fermentative hydrogen production processes are restricted by the existing metabolic pathways to 2 or 4 mol H<sub>2</sub>/mol glucose consumed, for butyrate or acetate fermentation, respectively. The techniques already discussed in Section 13.3.6 could not increase yields beyond these limits. In practice, typical yields in the range of 1 to 2 mol H<sub>2</sub>/mol of glucose result in 10–20% chemical oxygen demand (COD) removal, since the main part of the organic content of the wastewater remains in the liquid phase in the form of various VFAs and solvents. Even under optimum conditions of 4 mol H<sub>2</sub>/mol glucose, about 60–70% of the organic matter of the feed remains in solution (Venkata *et al.*, 2008; 2009). Further utilization of the organic matter contained in the effluent of a fermentative hydrogen producing bioreactor, could increase the overall energy output of the substrate to hydrogen and organic acids in the first stage and additional energy extraction by feeding the effluent of the first stage reactor to a second stage.

One approach to utilize/reuse the remaining organic matter in producing a second useable form for energy (an energy carrier) is to produce  $CH_4$  in a second stage. Integration of an acidogenic process with a subsequent methanogenic process for combined hydrogen and methane generation, offers several advantages such as a higher performance of the process in terms of waste stabilization efficiency and net energy recovery (Ghosh *et al.*, 1985). Such a two-stage system has been proposed so far for organic solid wastes rich in carbohydrates such as food wastes (Han and Shin, 2004), cheese whey (Antonopoulou *et al.*, 2008a; Venetsaneas *et al.*, 2009), olive mill wastewaters (Koutrouli *et al.*, 2009), household solid waste (Liu *et al.*, 2006b), a mixture of pulverized garbage and shredded paper wastes (Ueno *et al.*, 2007a) and wastewater sludge (Ting and Lee, 2007). A combined hydrogen- and methane-generation process has already been

scaled up to the pilot plant stage, for organic solid wastes (Ueno *et al.*, 2007b). The hydrogen and methane production rates were 5.4 m<sup>3</sup>/m<sup>3</sup>/d and 6.1 m<sup>3</sup>/m<sup>3</sup>/d, respectively while the process COD removal efficiency was 80%. The overall efficiency of this combined process is demonstrated by the fact that methane yields were twofold higher than a comparable single-stage process (Ueno *et al.*, 2007b).

Another approach to increase the overall energy extraction is to couple the fermentative hydrogen production with photofermentation with the aim to recover additional hydrogen. In such a two-stage process, the rich in organic acids effluent of fermentation which is produced in the first stage by anaerobic fermentative bacteria could be converted to hydrogen in the second step by non-sulfur purple photosynthetic bacteria which capture light energy, using a photobioreactor. This combination of both kinds of bacteria not only reduces the light energy demand of the photosynthetic bacteria but also enhances the hydrogen yield as well (Das and Veziroglu, 2001). Intensive research has been carried out in this area (Nath et al., 2008; Chen et al., 2008b) in the last few years. However, there are important factors limiting the practical application of such a process. One of them is that the involved hydrogen enzyme, nitrogenase, is potentially sensitive to the nitrogen content of the medium/substrate since nitrogen inhibits enzyme activity, as well as represses nitrogenase synthesis. However, this limitation can be potentially overcome either by genetic manipulation (Drepper et al., 2003) or selection (Rey et al., 2007) to remove nitrogenase regulation. In addition, one of the most severe constraints is that photosynthetic efficiencies are very low since at even moderate light intensities, the main part of captured light is dissipated as heat (Hoekema et al., 2006). This means that there will be a demand for large surface areas for the production of hydrogen contributing to the total cost and render the development of a two-stage process of fermentation-photofermentation, far from practical application.

Another approach to increase the overall energy recovery could be the coupling of fermentation with the additional hydrogen production, via a MEC. In this twostage system, the organic acids which are typical by-products of hydrogen fermentation will be converted to hydrogen in a MEC (Liu *et al.*, 2005; Rozendal *et al.*, 2006). Specifically, the electrogenic bacteria, catabolize the substrates and use the anodic electrode as terminal electron acceptor while supplementary voltage (>200 mV) is added in order to drive hydrogen evolution at the cathode. Thus, a sequential second stage of a MEC after a fermentative hydrogen production first stage could completely convert the effluent of first step to hydrogen, achieving in principle, 12 mol H<sub>2</sub>/mol glucose with only a small electricity supply. However, the fact that the yields for MEC which have already been reported in the literature are quite lower than the respective yields of dark anaerobic fermentation process, in combination with the high cost of cathodic electrodes and the reduction of the electrical input, limit the practical applicability of this promising technology.

### 13.3.8 Pilot plants in fermentative hydrogen production process

Up to now, a continuous scaled-up process for sustainable fermentative  $H_2$  production has not been reported in the literature. Only very few studies, are available so far, regarding the fermentation of sugars to hydrogen, at pilot scale. Ren *et al.* (2006) performed a pilot scale study in a continuous flow anaerobic fermentative reactor with an active volume of 1.48 m<sup>3</sup> and using molasses as substrate. The reactor operated under the organic loading rates of 3.11-85.57 kg COD/m<sup>3</sup> reactor/d and produced 5.57 m<sup>3</sup> H<sub>2</sub>/m<sup>3</sup> reactor/d or 8240 L H<sub>2</sub>/d with a hydrogen yield of 26.13 mol/kg COD removed. The effluent which was produced, contained primarily acetate and ethanol and was as high as 3000 L/d. This, rich in acetate, effluent could be further exploited for hydrogen production through a subsequent photoeterotrophic stage, which could increase hydrogen production by 317%.

Vatsala *et al.* (2008) evaluated the feasibility of hydrogen production from a sugar cane distillery effluent using co-cultures of *Citrobacter freundii* 01, *Enterobacter aerogenes* E10 and *Rhodopseudomonas palustris* P2, at 100 m<sup>3</sup> scale. The reactor operated at batch mode for 40 hours, and the hydrogen production was 21.38 kg with an average yield of 2.76 mol H<sub>2</sub>/mol glucose and a rate of 0.53 kg/100 m<sup>3</sup>/h. The results showed that distillery effluent could be used as a source of hydrogen providing insights into treatment for industrial exploitation.

Since data for real applications are not available so far, we can design such a process based on the respective lab-scale experiments. The problem is that the hydrogen productivity and yields depend significantly on the prevailing conditions, the feedstocks as well as the inoculum used. However, from laboratory-scale work on continuous processes, it could be suggested that such a process may operate at a mesophilic temperature, at a pH around 5.5 and an HRT approximately 8–12 hours, for simple substrates. Higher HRTs are indicative for complex carbohydrate-rich feedstocks. Finally, such a process or the indigenous microbial species available in the feedstock/waste, which has often proved to work optimally (Antonopoulou *et al.*, 2008a; 2008b).

### 13.3.9 Modelling and optimization of the process

Despite the multitude of studies on fermentative hydrogen production, the kinetic models which have already been developed or used to describe the process are limited. This is due to the fact that hydrogen production and metabolic products distribution is affected by many factors and up to now, the role of each is not well understood. So, there is a lack of models which incorporate important parameters such as pH, hydrogen partial pressure and regulation mechanisms like the ratio of NADH/NAD<sup>+</sup>, influencing hydrogen production and products' stoichiometry.

The majority of the researchers have used simple models in order to describe their experimental data. For example many of them have used the modified Gompertz equation developed by Zwietering *et al.* (1990) to predict hydrogen evolution in batch tests, using different substrates and inocula (pure or mixed cultures) (Lay *et al.*, 1999; Chen *et al.*, 2002; Wu and Lin, 2004; Fang *et al.*, 2006). However, this equation cannot be applied in continuous systems, and it cannot predict the concentrations of substrates utilized and those of metabolites produced along with hydrogen.

Recently, researchers have used more complicated models, such as modified versions of the IWA Anaerobic Digestion Model No.1 (ADM1) (Batstone et al., 2002). The latter is a widely applicable mathematical model, which was developed for describing the anaerobic digestion process. The application of ADM1 to nonmethanogenic systems demands modifications, since the initial model structure uses constant-stoichiometry to describe product generation from carbohydrates fermentation as well as excludes lactate and ethanol – two important metabolic products - from its structure. Lin et al. (2007) used modified ADM1 to describe glucose metabolism and products distribution (butyrate, acetate and ethanol) by selected clostridium species in batch cultures. Rodriguez et al. (2006a; 2000b) proposed an initial model to mechanistically describe formation of products in anaerobic fermentations and the predictions of this model were integrated in ADM1 as a variable stoichiometry function. Penumathsa et al. (2008) modified ADM1 in order to apply it to continuous bio-hydrogen production systems using a variable stoichiometry approach derived from experimental information. The simulation results obtained, provided good predictions of the dynamics in a continuous bio-hydrogen production reactor fed with sucrose, over a wide range of influent substrate concentrations. However, the modified ADM1 cannot predict and simulate the distribution of products from glucose metabolism under different environmental conditions. So, the induction of a proper regulating mechanism to regulate the fractionation of monosaccharides depending on hydrogen partial pressure, temperature, pH, etc. should make the model more robust and reliable for describing continuous fermentative hydrogen production systems.

#### 13.4 Hydrogen economy

The main advantage of biohydrogen is that it is a clean,  $CO_2$  neutral energy source, which can be used in fuel cells to produce electricity efficiently and water as a by-product, compared to other fossil fuels, the oxidation of which is accompanied by  $CO_2$ ,  $NO_x$ , particulate and other emissions. Moreover, the high efficiency of electricity generation in fuel cells that utilize hydrogen is independent of the scale of the fuel cell. This feature allows the application of fuel cells (and consequently, the use of hydrogen) at both large scale (e.g. industrial plants) and small scale (e.g. vehicles) (Gosselink, 2002). In biohydrogen processes, the energy of sunlight is first captured in the plant biomass and then transferred to  $H_2$  as an energy carrier or is directly harvested in the form of  $H_2$ . The chain of sunlight energy to hydrogen production and then hydrogen storage and distribution to the ultimate electricity generation comprises a sustainable energy scheme, which can be applied to replace gradually the fossil fuel economy. Technological advances reducing the limitations of biohydrogen processes could render the hydrogen economy easier to implement.

There are few economic analyses in the literature about hydrogen production. Most studies have been conducted at lab scale, while problems related with scaling up have not yet identified. Ressnick (2004) performed a comparative economic analysis applying a series of economic models to predict the capital and operating costs of the various approaches having been tested at a lab scale. The estimation has been based on a capacity of 50 million SCFD (standard cubic feet per day) and, based on the specific hydrogen production rate reported in the literature for the various biohydrogen processes considered, the size of the plant was assessed (Table 13.7).

The capital cost is mostly affected by the land area required in every approach. The annual sunshine limitations have not been taken into account in this analysis, and this has an impact on all photo-dependent processes. The specific rate of hydrogen production is also crucial in the above analysis. Any increase or decrease of these values would dramatically affect the economic analysis. As a result, more efficient bioreactor designs that could improve the rate and decrease the reactor volume, shrinking the capital cost further.

	Specific H <sub>2</sub> production rate (mmol/L/h)	Capital costs* \$/GJ/y	Operating costs \$/GJ
Direct biophotolysis			
(in a tubular reactor)	0.07	1 220	11 170.33
Indirect biophotolysis (in open ponds + dark fermentation + photo fermentation)	0.355	2.40	16.26
Water–gas shift (in spiral PVC tube bioreactor)	96	4.20	25.23
Photofermentation (closed photobioreactor)	153	1.41	30.70
Dark fermentation (in a fixed bed)	121	0.64	155.59

Table 13.7 Economics of different hydrogen production processes

\* Allowing a 90% economy of scale for the bioreactors, but not allowing a scale factor for the price of land. A 20 year linear depreciation of the investment has been assumed.

The operating costs also vary significantly depending on the biotechnology used. The high operating costs of direct biophotolysis are attributed to the labour costs associated with the large land area involved. In the case of the water–gas shift and the photo and dark fermentation technologies, the cost of the feedstock is crucial. If the cost of CO and glucose is excluded from the analysis, the operating costs of these technologies would decrease to 17.44, 5.60, 4.43 \$/GJ respectively.

## 13.5 Advantages and limitations

The main barriers for applying fermentative hydrogen production as outlined in any economic analysis are the low yield of hydrogen, low production rates and the cost of the feedstock. In order to make the biohydrogen economy viable there is a major challenge to increase the yield and production rates through:

- 1. Overcoming the light saturation effect. In the light-driven processes the conversion efficiency of the solar energy to hydrogen is estimated to be 10% (Hallenbeck and Benemann, 2002). This estimation is considered to be optimistic since it is based on data obtained under low light conditions that favor the dark reactions, the rate of which is limiting. Under full sunshine, the mechanism for electron transfer in algae is ten times slower than that of the light capture. As a result 90% of the photons captured decay as heat or fluorescence. The so-called light-saturation effect also applies to the photosynthetic bacteria. To overcome the light-saturation effect, the efficiency of the process can be increased through application of suitable mixing patterns that would reduce the time of exposure to the intense light and increase the nutrients transfer, design of reactor configurations that would dilute the light fall on the algal surface, as well as development of algal mutants that would absorb and waste fewer photons (Hallenbeck and Benemann, 2002).
- 2. Improving the dark fermentation technology. Rapid gas removal and separation as well as bioreactor design enhance the yield and production rates of hydrogen. To keep  $CO_2$  and  $H_2$  at low concentration, rapid removal of these two gases is required and  $H_2$  purification to concentrate and remove CO traces that would contaminate PEMFCs is necessary. Techniques of removal of  $H_2$  and  $CO_2$  have already been presented in Section 13.3.6.
- 3. Improving the CO–water shift reaction. Levin *et al.* (2004) consider the CO– water shift reaction carried out by certain heterotrophic bacteria promising. However, in the case of the CO–water shift reaction, the supply of the CO gas in a large volume reactor may require new bioreactor design to facilitate the mass transfer and contact between bacteria and the gas.
- 4. Integration of bioprocesses. Integrated strategies consist of two steps, with the first one being the fermentative hydrogen production, and the second one being either photobiological hydrogen production or methane production or MEC for hydrogen production as already discussed in Section 13.3.7.

Apart from the limiting factors concerning the biohydrogen process technology, there are other important parameters that affect the economy of hydrogen. For example, the limited availability of infrastructure for the transport, distribution and storage of hydrogen. The traditional options for hydrogen storage are cylinders of pressurized or liquid gas which is very problematic in the case of hydrogen gas. Although hydrogen has a very good ratio of energy to weight, it has a poor ratio of energy to volume compared to other fuels (hydrocarbons), therefore large tanks are required. Application of pressure to reduce the volume or liquefaction may result in smaller tanks but these technologies are energy consuming. On the other hand, for transportation use, storage meets limitations of volume and weight, while sufficient fuels must be available to secure the vehicle autonomy over long distances compared to the gasoline. Another option of hydrogen storage is the physical (adsorption on metal hydrides) and chemical storage (formation of alkali metal hydrides). Nanostructured materials are another promising alternative since they ensure high capacity. Transfer through a pipeline grid is another option but there is a question about whether the existing gas pipeline systems can be used for hydrogen supply. The quality and condition of the material of the pipeline should be checked since any metallic components may be affected by the hydrogen. Parts of the pipeline as the welds, valves and flanges should also be checked for their ability to hold the hydrogen.

## 13.6 Future trends

Today, hydrogen is used mainly in the petrochemical industry or as a feedstock in the industry, but not as an energy carrier. For this, the development of the supply sector (production and distribution-transportation-storage) and the end-user application should evolve simultaneously. The high investment costs required for this venture would be counterbalanced by strong driving motivations such as (Groot, 2003):

- The use of hydrogen in an efficient and clean electricity process such as PEM fuel cells.
- The use of hydrogen as a fuel for vehicles (storage of hydrogen is an issue, especially for the small compact vehicles).
- The use of hydrogen as an energy carrier through conversion of the electrical energy generated by renewable resources (solar energy, wind power) to chemical energy in the form of hydrogen (via electrolysis). This will replace the need to store large amounts of electricity directly.

## 13.7 Sources of further information and advice

For MEC technology: http://www.engr.psu.edu/ce/enve/logan/journal publications .htm

- For MEC technology: http://www.engr.psu.edu/ce/enve/logan/bioenergy/research\_ mec.htm
- For MEC technology: http://www.fctec.com/fctec\_types\_pem.asp
- IEA Hydrogen Program: http://www.eren.doe.gov/hydrogen/iea/
- EU Cost action 841: http://lbewww.epfl.ch/COST841/home.html
- HyNet. The European Thematic Network on Hydrogen: http://www.hynet.info/
- Hydrogen Information Network: http://www.eren.doe.gov/hydrogen/The 'National Hydrogen Energy Roadmap'
- ESF/PESC Network 'Biomass Fermentation Towards Usage in Fuel Cells' http:// www.bfcnet.info/

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## Production of bio-oils via catalytic pyrolysis

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Abstract: This chapter provides a review of catalytic pyrolysis summarising the potential of the methodology. Catalytic pyrolysis is centred on the use of catalysts in the production of bio-oils and related oils by pyrolysis of biomass and various waste materials. The subject is detailed against growing requirements for development of sustainable energy and fuel sources as pressures on fossil fuels increase as well as increasing fears on climate change and potential fuel shortages. The economics of pyrolysis derived bio-oil production against competing established and emerging technologies is provided. The review summarises the current state-of-the-art with particular reference to the challenges of catalysing reactions in the harsh environments of pyrolysis reactors. The types of active solid materials that can be used to generate oil are detailed so as to indicate the flexibility of the methodology. The outlook for commercialising of the technology is also summarised. A brief review of the potential use of pyrolysis products is given and barriers to uptake of this emerging technology are explained.

**Key words:** pyrolysis, catalytic pyrolysis, zeolites, mesoporous silicates, transition metal catalysts, bio-oil, pyrolysis-oil.

#### 14.1 Introduction

There is little doubt that the world is facing an uncertain future around the continued use of fossil fuels as has been outlined previously in this book and elsewhere.<sup>1</sup> Fossil fuel related climate change due to anthropogenic emissions of carbon dioxide is well known with 98% of carbon emissions arising from fossil fuel combustion.<sup>2</sup> Further, depletion of fossil fuel reserves is expected within a few generations<sup>3</sup> and energy security has become a major issue.<sup>4</sup> Whilst the major uses of fossil fuels are in domestic energy production<sup>5</sup> and transportation,<sup>6</sup> petroleum, gas and coal have very significant other uses. For example, oil is used to prepare in excess of 70 million tonnes of polyolefins per year.<sup>7</sup> Perhaps most importantly, very significant amounts of gas and oil are used in the production of fertilisers.<sup>8</sup> Fertiliser is wholly necessary for maintaining food supplies and feeding the growing world population. Fertiliser is prepared via the fixation of nitrogen by reaction of atmospheric nitrogen with hydrogen over transition metal catalysts, usually using iron based catalysts as were originally developed by Haber and Bosch.<sup>11</sup> The product of the reaction, ammonia, can be subsequently oxidised to nitric acid and the direct reaction of further ammonia yielding ammonia nitrate and this has been the basis of the modern fertiliser industry for almost 100 years.<sup>12</sup> The hydrogen needed in ammonia synthesis is derived from nickel catalysed reactions of gas or oil with water (steam reforming<sup>13</sup>) followed by a copper-zinc oxide catalysed reaction of carbon monoxide with water (water gas shift<sup>14</sup>). These reactions are outlined further below. Because of the hydrogen sources used, the fertiliser price is closely related to the oil price.<sup>9</sup> It should be noted that alternatives to steam reforming exist and hydrogen can also be obtained from methane by decomposition<sup>15</sup> and aromatisation.<sup>16</sup> Because hydrogen is essentially derived from fossil fuels (either directly, as detailed here, or indirectly via electrolysis of water using convention fossil fuel energy sources), it seems appropriate that, for the purposes of this review, hydrogen is considered as a petroleum product.

The over-reliance on fossil fuels derives from the convenience of these energy sources as a means of transporting and delivering energy.<sup>17</sup> Alternative sources of energy (wind, solar, nuclear, etc.) are unlikely to provide a convenient source of energy consistent with industry requirements and not precipitate large-scale industry changes and the capital required to replace current large scale chemical technologies based on oil processing that supply polymers, fertiliser, fine chemicals, etc. An alternative strategy to drastic modification of the chemical economy and the use of oil as a form of transporting energy is to find an effective means to generate petroleum-like products from renewable or waste material sources. The potential of pyrolysis is one means to affect the delivery of both petroleum and hydrogen allowing maintenance of current technologies.

#### 14.2 Pyrolysis: a brief background

Pyrolysis is a term used to describe the effect of heat on a substance such that no or little external oxidation or hydrolysis occurs. In this way, the pyrolysis can occur in an ambient environment provided combustion does not occur. Recently, the term pyrolysis has been associated with the development of an alternative means to recover energy from organic materials and is one of several possible strategies to develop energy sources from renewable sources rather than fossil fuels. There are biochemical methods for producing bioethanol as an energy source and these are based on either direct fermentation techniques for sugar rich crops or fermentation combined with chemical treatments for more woody and low-sugar plants.<sup>18</sup> This traditional sort of fermentation process to produce bioethanol is often described as a first generation biofuel technology. Other first generation biofuel technologies include transesterification (e.g. the reaction of vegetable oil with an alcohol) and biological anaerobic digestion of biomass. Despite the modern policy driven trends towards the use of bioethanol as a fuel or fuel additive<sup>19</sup> there is a conflict between the use of what are essentially edible crops and food security.<sup>20</sup> The use of lignocellulosic materials as a potential biofuel source would do much to prevent fears on shortages of food that might arise as arable land is used to generate fuels rather than foods. Despite the clear need to develop low quality crop fermentation, the science is not facile and

chemical/bio pre-treatments and designer yeasts are being developed to allow this technology to be delivered.<sup>21</sup>

Pyrolysis is one of a related series of thermo-chemical methods to extract energy from organics that rely on heating them and effecting a conversion of the materials. The most direct thermo-chemical method is combustion where the materials are heated in excess oxygen to form carbon dioxide, water and heat (from the highly exothermic reaction). The combustion reaction may be catalysed to maintain lower flame temperatures thereby limiting oxidation of nitrogen and the production of nitrous oxide pollutants.<sup>22–24</sup> Energy can be recovered from the exothermicity of the combustion reaction in several ways. These include heat to drive turbines, the volume expansion deriving from the liquid expansion to gas as well as from high pressure steam raised in the combustion. Partial oxidation, when the oxygen used is significantly below that needed for complete oxidation, is described as gasification as it yields light fuel gases and CO and H<sub>2</sub> known as syn(thesis) gas (from its use in the industrial synthesis of methanol). Catalysts and conditions (flow, pressure, contact times) can be used to control the gas products that result from this controlled oxidation.<sup>25</sup>

Pyrolysis is the heating of the organic materials (biomass, waste food, waste plastic, etc.) in the absence (or at partial pressures and/or temperatures where reduction rather than oxidation is favoured) of oxygen. Pyrolysis produces a range of products including solids (char), which is charcoal like and can be used for solid combustion systems, liquid (tar) and gaseous products both of which can also be used for energy storage, generation and transportation although the char usually requires further upgrading for optimum use.<sup>26–29</sup> The volatile, but readily condensable, components are sometimes described by the term bio-oil or pyrolysis-oil. These terms are used because they reflect the possible use of the product as a replacement for petroleum in automotive and energy applications. The mechanisms involved in pyrolysis are exceedingly complex involving free-radical reactions.<sup>30</sup> They are briefly summarised below.

As detailed above, pyrolysis is a complex process with products varying considerably according to the temperature and pressure used. This is because the reaction involves several different chemical reactions in both the gas and condensed phases and there are further heat and mass transport limitations which prevent an accurate representation by equilibria.<sup>31</sup> One of the challenges in delivering cost-effective commercial technologies is modelling these complex kinetic processes which are necessary for the design of efficient plant.<sup>32</sup> Because of this, the reaction products depend not only on the temperature and pressure but also on the rate of increase of temperature and the residence time in a reactor.

The main product of a pyrolysis reaction can be written as:

Organic feedstock  $\rightarrow$  char + volatiles

The organic feedstock (see below) can be anything from biomass (plants and other vegetation), vegetable oils, food waste, waste polymers, animal fats, etc.

The char is a carbon-rich, low hydrogen, ash containing solid.<sup>33</sup> It has many applications; as the name suggests as a coke substitute,<sup>34</sup> an advanced adsorbent<sup>35</sup> and as a soil additive to increase fertility.<sup>36</sup> The char can also be gasified by suitable oxidants and catalysts to provide a route to syn gas.<sup>37,38</sup> The volatiles are essentially a mixture of compounds that are condensable (in usual conditions) or non-condensable. The non-condensables are the basic components of syn gas, H<sub>2</sub>, CO, CO<sub>2</sub> together with methane and are normally referred to as gas or syn gas.<sup>39</sup> In general, the relative amount of the gas component compared to the condensable and solid (char) content increases with temperature.<sup>18,40,41</sup> The gas component is, possibly, an important part of the strategy in a move towards a 'hydrogen economy' but there are many competitive processes to be considered.<sup>42</sup> One of the more promising methods is the combination of pyrolysis with water gasification.<sup>43</sup>

In most cases, the most sought after component of a pyrolysis reaction is generally the condensable or liquid fraction because of its potential as a possible fuel in power stations or internal combustion engines.<sup>44,45</sup> The liquid fraction (or bio-oil) that results from pyrolysis is a complex mixture of chemicals and contains a range of molecular weights from light hydrocarbons through to molecular weights of 200+.46 The elemental composition of the liquid (which is often described as a biofuel because of the uses outlined above) is close to that of the biomass (or other material) feedstock.<sup>47</sup> The bio-oil is a mixture of an aqueous phase containing a variety of low molecular weight oxygenated organic compounds (methanol, ethanol, acetic acid, acetone, etc.) and a hydrophobic non-aqueous component consisting of heavier molecular weight oxygenates (e.g. alcohols, phenols, cresols), aromatics (e.g. benzene, toluene, indene) and polycyclic aromatic hydrocarbons (PAHs – e.g. naphthalenes, anthracenes).<sup>48</sup> The bio-oil, as-produced, can be burned in engines and turbines directly. However, it is relatively unstable, acidic (and, therefore, corrosive), of relatively low calorific value compared to petroleum oils and viscous. This ensures that it has limited application for direct use in turbines or engines<sup>49</sup> and much work has been carried out into developing methods whereby the product oil can be upgraded for practical use and this is an important application of catalytic pyrolysis.<sup>50</sup>

As briefly mentioned above, the temperature at which pyrolysis takes place plays an important role in the product distribution obtained from the pyrolysis reaction.<sup>51,52</sup> At lower temperatures (<600 K), formation of char is favoured whilst at higher temperatures (>800 K), increased reaction rates and the breakdown of C–C bonds lead to gas formation. Intermediate temperatures favour oil production. Experimentally, much time is spent varying temperatures and conditions in order to define conditions for optimum product distribution. As well as temperature, 'residence time' plays a major role in defining the product distribution. In a simple batch reactor, residence time has little meaning being simply the time over which the reaction is run. Simple batch reactors are of little practical use and, instead, flow-through reactors are used for most of the research being carried out both academically and industrially. In flow-through or continuous reactors, great care is required to control residence time and this is most important in reactions of this type where the products are kinetically not equilibrium defined. Whilst full discussion of this subject is beyond the scope of this review, it is generally found: that high residence times at lower temperatures favour char production, high residence times at higher temperature favour gas synthesis whilst low residence times at higher temperatures favour liquid production.<sup>26</sup> The requirement to control product distribution coupled to a need to generate technologies that can process industrially significant amounts of feedstock has led to several forms of pyrolysis which are often differentiated in the literature. They are differentiated by the heating rate used and the residence time in the reactor chamber. In a basic reactor for industrial use, the aim will be for the feedstock to pass through a heated zone, complete reaction and subsequently pass through separators and secondary reactors such as reformers and crackers to upgrade products.<sup>50</sup> The residence time of the reactor will be defined by the time feedstock spends passing through the pyrolysis chamber heated zone. The heating rate is defined as the time taken to reach maximum temperature although equilibrium with the chamber temperature is not always possible and effectively the feedstock maximum temperature may be less than the actual chamber temperature. The products and unused feedstock will be separated via cooling and condensation with an appropriate recycle if needed. A complete description of reactor design is given elsewhere.53

#### 14.2.1 Conventional pyrolysis

Demirbas and Arin have summarised the characteristics of each form of pyrolysis commonly used.<sup>54</sup> Slow or conventional pyrolysis is characterised by relatively low temperatures, slow heating rates and high residence times. The methodology has been used for the production of charcoal for centuries. The methodology is based on using large solid pieces of feedstock (since heating the solid can be performed slowly and there is no requirement for rapid heat transfer) and heating *in situ* to a set temperature for a period of time.<sup>55</sup> Heating rates are of the order of 1°C/min and residence rates around a few seconds or longer. Higher temperatures are around 600–700°C. Typical yields are around an equal division as solid, gas and liquid.<sup>54–56</sup>

## 14.2.2 Fast pyrolysis

To increase the amount of liquid product a technique known as fast pyrolysis (more properly defined as thermolysis since it is the thermal degradation of a chemical compound into a range of product chemicals) was developed in the early to mid-1980s.<sup>57–61</sup> The yield of oil or liquid can be as high as 80% of the feedstock biomass but is normally around 65–75%. The corresponding amounts of char and

gas are typically 10–25 and 10–20%, respectively. Fast pyrolysis processes occur in the time frame of a few seconds or less and the product range obtained is highly dependent on chemical kinetics as well as heat and mass transfer in the reaction chamber as discussed by Bridgwater.<sup>62</sup> The residence time of solid in fast pyrolysis is of the order of a few seconds or less with a heating rate of tens or hundreds of °C/s and the temperature range used is normally above 650–1000°C. Bridgwater and Peacocke have reviewed various forms of fast pyrolysis reactors.<sup>63</sup> It is clear, that to achieve such heating rates that these reactors will be considerably more complicated than for conventional pyrolysis. There are some obvious requirements for equipment used in fast pyrolysis and these are:

- 1 High heating rate to allow reactants to react in short periods of time and minimise char formation.
- 2 Very rapid heat transfer to allow feedstock to reach optimum temperature during their short residence time in the reactor.
- 3 Rapid cooling (condensation) of the pyrolysis products on exit from the reactor which prevents further reaction to char and tar-like materials.

It is difficult experimentally, as well as being expensive, to achieve the high heating rates required in static (batch) reactors. This is particularly true for the large scale reactors that would be required commercially. Whilst the heating rates may be achieved in small volume fixed bed reactors (fixed bed - the solid does not move) they can be more readily achieved if the feedstock is fed in and out of the reactor held at fixed temperature. This is achieved using a gas flow to suspend the feedstock solid. Probably the best design is a fluidised bed reactor (FBR).<sup>53,63</sup> Here, a particulate solid, such as fine sand, together with a powder of the feedstock is supported on a high velocity gas flow forming a fluid that can be passed trough the reactor.<sup>64</sup> The support solid is normally re-circulated through the reactor after separation of the products and this is known as the circulating FBR. The need to suspend the feedstock in the fluid requires that it is in the form of a fine particulate. This is also a necessity for rapid heat transport from the environment of the reactor to the solid. For these reasons the solid feedstock is normally ground or milled into particulates of the order of 1mm diameter or less. The FBR also facilitates the rapid cooling required to collect the bio-oil. Separation of char is usually achieved using cyclone technologies. Despite the apparent technical complexity, FBRs are well-established technology<sup>64</sup> and probably represent the most cost-efficient form of pyrolysis.65

#### 14.2.3 Flash pyrolysis

Flash pyrolysis is an extension to fast pyrolysis where heating rates reach around 1000°C/s. Flash pyrolysis has been reviewed several times.<sup>66–68</sup> The residence time of the solid is less than a second and depending on the type of reactor the temperatures can be as low as 500 or as high as 1200°C. The very high rate of

heating requires very rapid heat transfer from the reactor environment to the feedstock and, because of this, particle sizes of less than 0.5 mm but usually less than 100 um are required. The small particle sizes of feedstock also result in small particles of char and this is a major disadvantage of the technique.<sup>65</sup> Great care must be taken to remove particles of char from the as-produced bio-oil because it can catalyse polymerisation of some of the products and increased viscosity of the bio-oil.<sup>65</sup> The major advantage of flash pyrolysis is the improved energy efficiency of the process which can be in excess of 70%.<sup>69</sup> Although we have not discussed the efficiency of pyrolysis processes here, it should be noted that pyrolysis is a strongly endothermic process and energy must be supplied to affect the heating in the reaction. The source of energy for heating is the feedstock itself, either before or after pyrolysis. The challenge for engineers is to configure reactor technologies to minimise losses through heat recovery and other methods to allow efficient heating of the feedstock during pyrolysis. There are various reactor technologies used in flash pyrolysis and are briefly introduced below.

- 1 Fluidised bed and circulating FBRs: These are probably closest to integration into large scale commercial use, and large scale pilot plants have been demonstrated.<sup>70</sup>
- 2 Entrained flow reactor: This reactor has been scaled to allow pyrolysis of 500 kg/h of feedstock.<sup>71</sup> In this reactor a carrier gas and a combustion gas (to produce the pyrolysis temperature by combustion) are fed into a reactor tube and powdered feedstock is fed into the high flow gas stream. Whilst the design is relatively simple the use of carrier gas (usually nitrogen) is a disadvantage.
- 3 Vacuum pyrolysis: This is a relatively new technique where the sample is heated under vacuum; the vacuum removes pyrolysis generated volatiles which are then condensed to the bio-oil.<sup>72</sup> This technique results in low residence times and also allows for rapid separation of the oil and char. Its major advantage is that it can operate at relatively low temperatures of 500°C.
- 4 Rotating cone reactor: This type of reactor was developed by scientists in The Netherlands.<sup>73,74</sup> In the rotating cone reactor, biomass particles are fed to the bottom of a rotating cone with inert heat carrier particles and are pyrolysed whilst being transported spirally upwards along the cone wall. The advantage is the absence of a carrier gas and high oil yields.
- 5 Ablative pyrolysis: There are several versions of this methodology which varies considerably from the other techniques discussed. It consists of solid particles being exposed directly to heat via contact with a heated surface or radiatively.<sup>75</sup> The action of pressing the particles against the hot surface reduces heat transfer requirements.

The final type of pyrolysis often differentiated in the literature is catalytic pyrolysis, the main subject of this article. In reality this is not a completely different form of pyrolysis and can be used with the same type of reactors, etc. outlined above. Catalytic pyrolysis is outlined in depth below.

#### 14.3 Pyrolysis economics

In terms of pyrolysis being used to generate a suitable alternative to petroleum products, pyrolysis is seen as one of a family of more environmentally sound products compared to fossil fuel use. The main alternatives to fossil fuels are bioethanol, bio-diesel and bio-(pyrolysis oil). As briefly outlined in the introduction there are advantages and disadvantages of all of these. In economic terms, it is clear that bioethanol currently has a clear advantage over any second generation biofuels with bioethanol from Brazilian sugar cane being within a price range of  $0.20-0.30 \notin /1^{76}$  compared to ethanol from lignocellulose or other biofuels which are around  $0.80-1.00 \notin /1.^{76}$  Because of the cost of first generation bio-diesels (i.e. from vegetable or other plant oils) where production costs are  $0.35-0.65 \notin /1$ , bioethanol production has greatly outstripped biodiesel production.<sup>77</sup> The rate of growth of both of these is expected to increase as petroleum prices continue to increase but biodiesel has and will continue to rely on legislation and governmental support.<sup>78</sup>

One advantage that second generation fuels that are recovered from low cost sources such as wood or waste materials have is that raw material costs are significantly lower than vegetable oils or animal fats.<sup>78</sup> The cost of, e.g., rice husks is around 15–20 €/ton.<sup>79</sup> The drawback in the use of pyrolysis to obtain usable oil products from cheap feedstocks is the high capital, maintenance and labour costs associated with the technology.<sup>79</sup> However, as shown by Islam and Ani, provided large scale plants can be built, pyrolysis can be economic for as-produced pyrolysis oil and catalytically upgraded pyrolysis oil.<sup>79</sup> Another advantage of pyrolysis lies in the use of materials that can be grown on relatively poor land. The IEA report data that suggest that by 2030, biofuels will contribute around 7% of transport fuel usage.<sup>80</sup> This target can be achieved through conventional ethanol production but will significantly affect land usage with loss of pasture land to, e.g., sugar cane crops.<sup>81</sup> This fuel driven use of land must be balanced by growing fears of food security<sup>82</sup> and the availability of low value materials grown in non-arable areas can alleviate some of the fears associated with growth of fermentable crops. Pyrolysis also offers a considerable technical advantage as large-scale production of ethanol from lignocellulose is not generally thought possible within the next few years.<sup>83</sup> There are now a number of demonstration plants built in the EU and USA, one of the largest being at Bastardo (Umbria) Italy which has a maximum throughput of 650 kg/h and is funded by the EU for research purposes.

There are other technologies for producing energy and bio-oils from waste materials and biomass. These can be grouped into prospective and established technology areas. Amongst the prospective methodologies are microalgal, supercritical fluid techniques and liquefaction. Microalgal production of bio-oils has been known since the early 1950s<sup>84</sup> and is still an active area of research.<sup>85</sup> Here, algae (microrganisms that convert sunlight, water and carbon dioxide to

lipids or triaceylglycerol) can be used to effectively trap  $CO_2$  from emissions or organic degradation and can be harvested to yield up to 80% of their weight as oil. However, scale-up remains a problem and prices are not currently competitive with ethanol or plant oils. Supercritical fluids are being explored as potential technologies. They can be used to affect hydrolysis of biomass to a mixture of methane, carbon dioxide, carbon monoxide and hydrogen.<sup>86</sup> Supercritical-CO<sub>2</sub> is becoming an important industrial solvent (e.g. dry-cleaning, coffee extraction) because its 'solvency' can be controlled precisely through pressure. It has been used to extract useful products from biomass directly.<sup>87</sup> Liquefaction of biomass is another area of research that has shown some promise but the products are normally quite high in viscosity and usually needs reducing gases such as CO and H<sub>2</sub> to be present and this can further increase costs.<sup>88</sup>

Conventional technologies include (as mentioned above) various established catalyst methods. Combustion remains a proven technique and the combination of catalytic combustion with biomass gasification may afford opportunities to develop both sustainable and environmental friendly energy production.<sup>89</sup> The use of fluidised bed gassifiers has been shown to be commercially viable for biomass use as demonstrated by Hamelinck and Faaij.90 The product of the gasification is syn gas (together with char and some methane) which is then used to generate methanol which is a useful fuel with a higher octane rating than petrol. For economy, char and hydrocarbons must also be used and a boiler to capture heat in the combined process alleviates some of the cost burden.<sup>90</sup> Leduc et al. have shown that choice of site is all important in operating such plants economically.<sup>91</sup> Syn gas can also be used to create petroleum-like fuels via the Fischer-Tropsch process.<sup>92,93</sup> The product of the reaction is a distribution of largely aliphatic hydrocarbons. The Fischer-Tropsch process is an engineering challenge taking place at temperatures up to 300°C in pressures of up to 40 atmospheres. The catalysts, either cobalt or iron based, can have limited life and strongly effect the product distribution. Many of the challenges associated with catalysts for use in the high temperature, high hydrocarbon and high pressure environments needed for synthesis of oils via the Fischer-Tropsch process are the same when developing catalysts for catalytic pyrolysis.

#### 14.4 Catalytic pyrolysis: catalysis

Catalytic pyrolysis has been an area of research aimed at developing viable methods to improve the quality of products compared to normal pyrolysis. The role of the catalyst is two-fold. Firstly, it lowers the temperature of the pyrolysis process and unstable hydrocarbons combine to form increased amounts of oil. Secondly, the catalyst adds a 'cracking' effect which deoxygenates the pyrolysis products by accelerating carbon dioxide and, more hopefully, hydrogen production.<sup>94,95</sup> In this way, catalytic pyrolysis produces more hydrocarbon-like oil with lower tar and viscous content. Before detailing some of the current work

in the area of catalytic pyrolysis, it is worthwhile reviewing very briefly the fundamentals of catalysis so that the challenges faced by this particular technology can be properly assessed.

#### 14.4.1 Basics of catalysis

Catalysis is the foundation of the chemistry industry and is widely used in large scale synthesis of bulk chemicals and fine chemicals. It is the heart of the fertiliser, petroleum, polymer, inorganic and pharmaceutical industries amongst others and is of growing importance in environmental control including pollutant and waste mitigation, pollution ablation as well as in the generation of new alternative energy and fuel sources. A general review of catalysis is beyond the scope of this book but the reader is referred to a number of excellent books. Chorkendorff and Niemantsverdriet have recently reviewed the general area of catalysis<sup>96</sup> and Ertl et al. have edited a comprehensive summary of the state-of-the art.<sup>97</sup> Morris and others provide a preface to summarise recent work.98 The industrial perspective has been well reviewed by Rase99 whilst Cybulski and Moulijn have presented details of modern reactors and process design.<sup>100</sup> The import subjects of catalyst preparation and synthesis, which are pivotal in determining cost-effectiveness of the process and the efficacy of the catalyst itself, have been thoroughly summarised.<sup>101</sup> Finally, the theory of catalysis has been detailed in depth.<sup>102</sup> Catalytic mechanisms are normally defined by the adsorption and specifically the chemisorption of molecules at the catalyst surface.<sup>103</sup>

Catalysis has been divided into two separate subject areas. The first of these is homogeneous catalysis where the reactants and the catalyst are in the same phases, e.g. ion catalysed reactions in solution. The second area is heterogeneous catalysis, principally used in the manufacture of very large quantities of chemicals, organic and inorganic materials.<sup>104</sup> Here, the catalyst and reactants are in different phases most usually a solid catalyst and gas phase reactants. This is most useful for high throughput and is used for many of the very large scale processes carried out in industry including sulphuric acid, ammonia, methanol, nitric acid, ethylene oxide, cyanide synthesis as well as petroleum reforming and cracking, gasification, steam-reforming and water-gas shift processes.

As every high school student would know, a catalyst increases the rate of a chemical reaction without itself being consumed or altered in the reaction. This is a result of the catalyst interacting with the reactants to lower the activation energy barrier to the reaction. It does not alter the energetics (i.e. the free energy) of the reaction and so does not change the equilibrium between reactants and products directly. In the most obvious use of a catalyst, the rate of reaction is increased allowing increased rates of production at a particular temperature. Alternatively, the catalyst may be used by offsetting the increased rate of reactions that can be achieved (which can be orders of magnitude greater) against the process temperature used. This may be used to simply move a reaction into a feasible temperature range

where reactor engineering becomes practical. It can also be used to reduce the energy input required by endothermic processes allowing more economic operation. A simple example would be methane combustion which can be catalysed by a number of precious metals as well as lanthanide oxide materials.<sup>22–24</sup> The catalyst is used in gas turbines to lower combustion temperatures, thereby reducing the oxidation of nitrogen to nitrogen oxides. Similar reactions where that catalyst would be used to simply increase the rate of reaction in the formation of the thermodynamically stable product are the oxidation of CO and hydrocarbons to CO<sub>2</sub> as shown below.<sup>105</sup>

Practically, catalysis is often used in more complex ways so as to produce significant amounts of a product that would not be obtainable in an un-catalysed process. An example is the partial oxidation of ethylene to ethylene oxide:<sup>106</sup>

$$H = C = C H + 0.50_2 \rightarrow H - C - C H H H$$

This is the reaction which is mildly exothermic and the ethylene oxide formed is a partial oxidation product. The catalyst is not used to increase the rate of formation but rather to provide an operable process window at lower temperatures because at higher temperatures combustion of ethylene is highly favoured and the ethylene oxide would be a very short-lived and unrecoverable intermediate. Industrially, the reaction is catalysed by silver supported on alumina although various promoters for the epoxidation reaction as well as total oxidation inhibitors are used as part of the catalyst formulation to ensure high selectivity. The reaction operates at around 250°C, a low enough temperature for the desired product to be separated.

As mentioned earlier, the Haber-Bosch process has been used for the synthesis of ammonia from nitrogen and hydrogen for many years:<sup>11</sup>

$$N_2 + 3H_2 \rightarrow 3NH_3$$

This is an exothermic, thermodynamically favoured process but is kinetically limited. The reaction is catalysed by a potassium promoted iron catalyst. In simplistic terms, the catalyst is used to allow low temperature dissociation of nitrogen, the main activation energy barrier in the reaction. However, this is an equilibrium process and as the temperature is increased, the equilibrium favours the reactants (le Châteliers principle). In this way, although a catalyst does not alter the equilibrium in a chemical process, in this case the catalyst allows a low temperature (400°C) to be used and, thus, a higher equilibrium concentration of the product ammonia to be achieved. An un-catalysed mixture of hydrogen and nitrogen would reach the same equilibrium concentrations but would take considerably longer and not be consistent with the continuous process needed for large volume manufacture. The use of catalysts to effectively control equilibrium and rate is further illustrated by the water gas shift reaction:<sup>107</sup>

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$$CO + H_2O \rightarrow CO_2 + H_2$$

This process is also mildly exothermic and equilibrium limited and like ammonia synthesis, the equilibrium favours reactants at higher temperatures but is kinetically limited requiring a catalyst to be used to achieve reasonable rates at temperatures below 1000°C. In order to achieve a high rate of reaction it is carried out in two different stages. The first is high temperature shift (HTS) using an alumina supported nickel catalyst at around 400°C which yields high rates of reaction. The second, low temperature shift (LTS) process uses an alumina supported copper based catalyst at around  $200^{\circ}$ C – the lower temperature allows almost complete recovery of the valuable hydrogen product at the equilibrium limit. The shift reaction(s) also demonstrates how important the synthesis of the catalyst is in these high volume processes since that catalyst must have sufficient activity and lifetime to be cost-effective. The subject of catalyst design and manufacture is briefly outlined in this review because in catalytic pyrolysis the catalysts used face very challenging environments.

In very general terms, the catalyst functions by reactant molecules interacting with the surface and becoming 'activated' in some way. Understanding how and where these reactions occur on the catalyst surface has been the subject of intense research and most researchers use an active site concept where specific arrangements of surface atoms or defects in the surface provide locations for adsorption/activating of reacting species.<sup>108</sup> Very often, catalytic activity can be a unique property of a certain metal, oxide or combination. In order to maximise the number of collisions with the surface, it is usual to provide the active component with as high a surface area as is possible. This is normally achieved using an inorganic 'support' over which the active component is 'dispersed'.<sup>109</sup> This allows very high surface areas of what are sometimes quite expensive materials (e.g. precious metals) to be achieved at relatively low amounts (below 5% by weight of the support) and at sustainable costs. The inorganic support is designed to be thermally robust and plays little part in the catalysis reactions although metal-support interactions between an active metal component and a support oxide have been well documented.<sup>110</sup> In many cases the support is designed to be porous in order to provide as great a surface area as possible.<sup>111,112</sup> Despite the fact that theoretically catalysts are unchanged by the reaction it promotes, their performance is often assessed by their lifetime in practical use. The lifetime is defined by the period in which its rate lies within an acceptable performance level (i.e. rate of production). Very often, the rate decreases with time and although this can be compensated by increasing reactor temperature, there is a point where practically an upper operating temperature is reached. A too higher temperature might be manifest as an unacceptable amount of side products -i.e. the reaction selectivity is compromised. Alternatively, the temperature may rise beyond process variables to protect plant and safety. This decrease in activity largely results from two different processes occurring during use. These are sintering and poisoning.113-115

Sintering is a complex process whereby loss of surface area is observed through thermal treatment which promotes mass transport and particle agglomeration or loss of pore structure. Pores play an important role in catalysis as they allow access to internal surfaces and can promote size controlled reactions where the molecules restrain the molecules that can enter the pore system. The process of sintering is thermodynamically favoured because it results in lower surface area and consequent decreases in the free energy of the system. Highly dispersed and supported active materials (as crystallites or particles) grow by a diffusion mechanism into larger particles. Other high temperature processes may also be responsible for sintering including solid-state reactions, new phase precipitation (e.g. in the thermal phase transformation of high surface area  $\gamma$ -alumina to low surface area  $\alpha$ -alumina) and the crystallisation of amorphous silica supports.

Poisoning generally describes the adsorption of strongly held species at the active catalyst sites. These passivate the surface to the desired catalyst mechanism. This results in deactivation as either reduction in production rate or as loss of selectivity to the required product. Common poisons include S, P and Cl. These are normally adsorbed from contaminants in the gas phase and sacrificial adsorbents can be used to reduce the concentration of these.<sup>116</sup> More importantly for pyrolysis catalysts, carbon is also as an important poison and arises from hydrocarbon at the catalyst surface. Extensive carbon formation can leave to 'coking' where thick carbon deposits are formed. This coking can also be useful in oil chemistries because it can lead to useful liquid (resids) formation.<sup>117</sup>

# 14.5 Catalytic pyrolysis for improved pyrolysis-oil generation

The introduction of catalysts into pyrolysis processes introduces additional costs. Islam and Ani have estimated that the cost of catalytic pyrolysis process (in terms of dollar per joule of energy produced from the oil) might be around twice that of a pyrolysis only process although this would decrease with increased scale of production.<sup>79</sup> The main reasons for the higher costs are associated with the catalyst and the additional capital and human infrastructure requirements. However, it does appear that costs of less than  $1 \notin /1$  may be achievable<sup>118</sup> and this could ensure process viability as an alternative to petroleum. These and similar cost analysis do point to an important critical step in the introduction of this technology, the need to develop catalysts that demonstrate good performance and extended lifetimes or simple catalyst regenerative processes. This was also a key finding of a report by the NREL (National Renewable Energy Laboratory) in the USA.<sup>119</sup> This report provides an excellent summary of the research up to 2003 and there are other general reviews of catalytic pyrolysis which are useful including work by Bridgwater,<sup>47</sup> Elliott,<sup>120</sup> Sharma and Bakshi<sup>121</sup> and Chen *et al.*<sup>44</sup>

Although projected costs are higher there are a number of clear advantages in catalytic pyrolysis over conventional pyrolysis. These are:

1 The products have lower oxygen content and higher H:C ratios than simple pyrolysis-oil.<sup>122</sup> This is an important indicator of quality; the H:C ratio should be as low as possible for fuel use and an effective ratio is often defined:<sup>123</sup>

 $(H/C)_{eff} = (H-X)/C$ 

where H and C are the number of hydrogen and carbon atoms in the product respectively. If X is the relative (to the value of C) number of hydrogen atoms in the original feedstock, then the effective ratio indicates the 'upgrading' of the catalytic pyrolysis product.

- 2 The product distribution is narrowed, i.e. the produced oil has a narrow molecular weight range consistent with use as a fuel oil with better yields in the gasoline ( $C_5-C_{12}$  range).<sup>124,125</sup> The catalytic action allows some control over the product distribution and by correct choice of catalyst and process conditions products of increased value can be increased in concentration.<sup>126</sup>
- 3 Catalytic pyrolysis increases the amount of aromatics and branching in the pyrolysis oil products compared to conventional pyrolysis methods.<sup>122,127–129</sup> This is extremely important to the potential use of pyrolysis oil as a fuel in engines and turbines because the presence of aromatics and highly branched hydrocarbons increases the smooth running of the engine or turbine. By use of catalytic techniques the aromatic content can be increased to 30–50% with the major products being naphthalenes and toluene but there are significant amounts of benzene, indanes and substituted benzenes.
- 4 The pyrolysis oil product from a catalysed process (rather than non-catalysed process) is deoxygenated significantly lowering the average oxygen to carbon ratio across the product distribution.<sup>46,130–132</sup> This is important for two main reasons.<sup>133–134</sup> Firstly, simple, non-upgraded pyrolysis fuels have low energy content which makes them unsuitable for direct use in established liquid hydrocarbon fuel technologies. Secondly, non-upgraded pyrolysis oils are highly acidic (as above) because of the oxygen content (around 40–50%) and removing oxygen significantly reduces the acidic components and decreases the corrosive nature of the product.
- 5 Catalytic pyrolysis also decreases the char content of pyrolysis products<sup>135</sup> whilst increasing the contribution of gases.<sup>136,137</sup> Reduction of char is extremely important as the presence of char can catalyse inter-molecular reactions during storage and increase product viscosity.<sup>138</sup>
- 6 The use of catalysts in a pyrolysis reaction can significantly lower the reaction temperature.<sup>139,140</sup> This is extremely important because pyrolysis reactions are endothermic and add significant costs to the overall process. Unlike most catalysis processes which are exothermic and can recover energy for any heating required, there is a true cost of running pyrolysis technology and it is, therefore, important to decrease the energy required as much as possible.

#### 14.6 Reactors for catalytic pyrolysis

There are many forms of reactors used for the study, analysis and large scale semicommercial testing in catalytic combustion. A full description of these is beyond the scope of this paper and the reader is referred to a number of papers. Samolada et al. have presented a typical laboratory set-up for gram quantities of biomass in a fixed bed reactor and this is very typical for small scale studies.<sup>133</sup> Numerous pilot plant size (kg type quantities) reactors have also been studied and these are largely centred on fluidised bed type systems.<sup>141</sup> These pilot stage systems will have hoppers and grinders for feeding real biomass samples (as particle size is critical in determining thermal transfer efficiencies), risers (for the fluidised bed generation), pyrolysis reaction chambers and systems for recovery and recycle of the catalyst. On the larger scale there are many variations of the methodology which allow product optimisation to different molecular weights as well as different products. The methods developed for commercial use and study have been summarised by Meng et al.142 These methods include, for example, catalytic steam pyrolysis where the addition of water promotes steam reforming reactions within the overall pyrolysis process. Quick contact cracking essentially involves a recirculating fluidised bed fast pyrolysis technique combined with a simple cracking catalyst which allows catalyst to be circulated in the fluidised bed and coke at the catalyst removed by oxidation during the recycle. The current development of large scale industrial plant is summarised by Dominov et al.<sup>143</sup> The results of a commercial trial of catalytic pyrolysis technology with emphasis on the design and construction of plant were reported by Xie and Wang.<sup>144</sup>

Despite the complexity of these technologies and individual reactor designs, simple representation of the main methodologies can be made and these are represented in Fig. 14.1. In the simplest fixed bed system (Fig. 14.1A), catalyst and powdered biomass or other hydrocarbons are mixed and the composite placed in a tube (held in place by ceramic wool or sinter disks). The tube is externally heated to produce a high heating rate. The pyrolysis reaction and the catalytic cracking/reforming reaction can also be separated into two separate processes (Fig. 14.1B). This allows the cracking/reforming reactions to be run at different temperatures as well as secondary input of gas (water, hydrogen) to improve that catalytic process. Fluidised bed reactors can also be run with an *in situ* (i.e. in the pyrolysis reactor) catalytic process (Fig. 14.1c) or an *ex situ* process. One of the biggest advantages of an *ex situ* process is that the catalyst can be used in a fixed bed which prevents the impact damage that occurs in a fluidised bed which can severely limit catalyst lifetime. Catalysts can be periodically regenerated by oxidative treatment to remove coke using a twin reactor tube.

#### 14.6.1 Reactions and mechanisms in catalytic pyrolysis

There is no uniform acceptance for the mechanisms involved in catalytic pyrolysis. This is probably because of the complexity of the process and the range of products



14.1 (A) simple fixed bed reactor. (a) is the carrier gas feed to remove products and (b) is the combined pyrolysis-catalysis reactor (tube). (c) are either sinter discs or ceramic wool. (d) is the hydrocarbon source mixed with catalyst. (B) is a fixed bed pyrolysis chamber and reactor (d/b) combined with a separate catalytic compartment (f). (e) is an inlet for catalysis process gas e.g. hydrogen or water. (c) and (d) are fluidised bed reactors. (c) and (b) are the reactor chamber and the bed material recirculation chamber respectively. (a) and (e) are the process gas for product recovery etc. and gas stream for catalyst treatment. (d) is the fluidised bed. In (c) the catalyst and fluidised bed support are recirculated. In (d) only the bed support is recirculated and the separate catalyst bed can be fed with a separate process gas (f).

formed which make quantitative analysis difficult. It is difficult to experimentally resolve intermediates in the reaction because of the number of different products formed and the conditions within reactors are not always amenable to characterisation by either *ex situ* or *in situ* methods. Further, the reaction temperature and pressure as well as the nature of the catalyst may change the nature of the reaction. Two mechanisms have become widely suggested as being the basis of pyrolysis. These are a free-radical mechanism and a carbonium ion mechanism and both of these are now very well established in terms of catalytic assisted cracking of hydrocarbons<sup>145</sup> and have been used to describe the mechanism of catalytic pyrolysis of biomass,<sup>146</sup> heavy oils,<sup>147</sup> natural oils<sup>149</sup> as well as various polymers.<sup>150,151</sup> Although these mechanistic models have been proposed since the 1940s and earlier, there has been little additional detail provided because of the experimental and analysis problems described earlier although Sakata *et al.* have extended the older models for the catalysed decomposition of polyethylene.<sup>152</sup> The *free-radical mechanism* is based

on a number of steps where high temperature homolytic reactions create free radicals; these free radicals are unstable and will have tendency to crack at  $\beta$ -bonds to form smaller hydrocarbons. Combination of free radicals allows recombination and, thus, some isomerisation. Water elimination, aromatisation, carbon oxide formation and hydrogen production follow from reaction of these radicals with each other or other hydrocarbon molecules. It is generally believed that the catalyst has a more profound effect on the initial free-radical generation step than the subsequent reactions since free-radical reactions are kinetically fast.

The carbonium ion reaction is similarly complex, involving carbocation formation and has been developed from early concepts into two distinctly different mechanisms. It should be noted that there is a confusion on the term carbonium ion. In the pyrolysis literature, few authors use the term correctly because the term is generally used to indicate any positively charged carbon atom. However, a carbonium ion is properly defined as penta- or tetracoordinated carbocation such as  $R_sC^{+,153}$  The first carbocation mechanism is described as monomolecular cracking.<sup>154</sup> Here, a penta-coordinated carbonium ion is formed from an alkane or alkane containing molecule group and this subsequently undergoes cracking and evolution of an alkene containing molecule or hydrogen. This reaction is considered relatively slow at lower pyrolysis temperatures and the second type of carbocation mediated reaction is probably more important; this is known as the bimolecular or  $\beta$ -cracking mechanism.<sup>155</sup> This process is initiated by a carbenium ion (a trivalent carbocation of type  $R_3C^+$ ) which subsequently undergoes hydrogen or hydride transfer followed by  $\beta$ -bond scission. Since the scission occurs with formation of an additional adsorbed carbenium ion, the mechanism is generally considered to be much faster than the monomolecular route.<sup>156</sup>

Separating the mechanism into two quite separate routes, free-radical and carbocation mediated, is probably not possible and both reaction mechanisms may contribute to the product formation although the relative importance of each is likely to vary with temperature. It has been found that the free-radical reaction will dominate at higher temperatures.<sup>147</sup> A term  $R_M$  has been used to describe the relative contributions of free-radical and carbocation mediated reactions in the cracking of heavy oils.<sup>147,148</sup>  $R_M$  can be estimated from the isobutane to normal butane ratio. When the  $R_M$  term (greater than 1.5) is high, the reaction will be dominated by the carbocation mechanism and when low (below 0.5) by the free-radical reaction mechanism. Intermediate values indicate that both reaction mechanisms are important. This may be rationalised in terms of the shorter lifetime of free-radical species which mitigate more complex rearrangements.

Whatever the nature of the reaction mechanism, it is clear that the catalysed pyrolysis of complex organics must involve a number of different reactions.<sup>146</sup> Following an early work by Chang and Wan in 1947<sup>157</sup> for the decomposition of triglycerides (see later chapters in this book for a more detailed review of the catalysis of triglycerides) these will involve reaction steps similar to those below (not inclusive of all possible reactions):

- 1 Degradation of the complex reactants to yield acrolein (CH<sub>2</sub>=CHCHO) plus various complex fatty acids and ketenes as well as other similar compounds (e.g. RCOOH, RCH=CO where R is an alkyl group).
- 2 Degradation of fatty acids and acrolein into carbon dioxide, water and alkanes, e.g.

 $RCOOH \rightarrow CO_2 + RH$  $2RCOOH \rightarrow CO_2 + RCOR$ 

3 Breakdown of ketenes, ketones and acrolein into carbon monoxide, light hydrocarbons and alkenes

$$2RCH=CO \rightarrow 2CO + RHC=CHR$$
$$CH_2=CHCHO \rightarrow CO + C_2H_4$$
$$RCOCH_2R \rightarrow R_2 + CH_2CO$$
$$2RCOCH_2R \rightarrow 2 R_2 + CO + C_2H_4$$

4 Decomposition of alkanes into hydrogen and carbon (principal char forming route)

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$$

5 Formation of alkenes from alkanes

 $C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$ 

6 Division of alkanes and alkenes into smaller alkane, alkene and di-alkene molecules, e.g.

$$C_n H_{2n+2} \rightarrow C_{n-m} H_{2(n-m)+2} + C_m H_{2m}$$

7 Growth of longer chain alkanes

$$\mathbf{C_nH_{2n+2}} + \mathbf{C_mH_{2m}} \rightarrow \mathbf{C_{n+m}H_{2(n+m)+2}}$$

- 8 Isomerisation of alkanes and alkenes
- 9 Aromatisation of alkanes and alkenes via reaction mechanisms such as the Diels-Alder reaction,<sup>149</sup> e.g.

$$C_n H_{2n+2} \rightarrow C_{n-6} H_{2(n-6)+1} C_6 H_5 + 4 H_2$$

10 Formation of alkynes from alkenes

$$\mathrm{C_nH_{2n}} \rightarrow \mathrm{C_mH_{2m-2}} + \mathrm{H_2}$$

11 Hydrogenation of alkenes and alkynes, e.g.

$$C_n H_{2n+2} + H_2 \rightarrow C_n H_{2n+2}$$

More generally, the types of reactions occurring in catalytic pyrolysis that are directly affected by the presence of the catalyst can be described in terms of more general mechanisms based on combinations of cracking, reforming and other reactions. Some of these are described above. The water gas-shift and similar reactions also clearly affect the gas composition. This more general description is useful because the pyrolysis temperature (whether pyrolysis and catalytic reactions are separate or integrated) is the most critical process parameter because the products of the thermal pyrolysis reaction are strongly dependent on the temperature and these gas products will strongly affect these catalysed reactions. In this way, the product distribution can vary considerably with temperature. These reactions are:

- 1 Classic catalytic reforming reactions such as isomerisation, cracking and aromatisation as described above. The role of the catalyst is based on dissociative chemisorption of the alkanes and alkenes forming chemisorbed hydrocarbon fragments and hydrogen. Recombination of fragments leads to formation of smaller hydrocarbons, isomers and aromatics as well as hydrogen.
- 2 Hydro-cracking where hydrogen produced in other reactions is used in the fragmentation of long hydrocarbon chains into smaller units, e.g.

$$C_nH_{2n+2} + H_2 \rightarrow C_{n-m}H_{2(n-m)+2} + C_mH_{2m+2}$$

3 Hydrogen can also be important in terms of dehydration reactions with the products of the thermal pyrolysis,<sup>158</sup> e.g.

$$\begin{split} & \mathrm{C_6H_8O_4}+6\mathrm{H_2} \rightarrow 6\mathrm{CH_2}+4\mathrm{H_2O} \\ & \mathrm{C_6H_8O_4}+4.5\mathrm{H_2} \rightarrow 6\mathrm{CH_{1.5}}+4\mathrm{H_2O} \\ & \mathrm{C_6H_8O_4}+3.6\mathrm{H_2} \rightarrow 6\mathrm{CH_{1.2}}+4\mathrm{H_2O} \end{split}$$

where  $CH_2$ ,  $CH_{1.5}$  and  $CH_{1.2}$  represent the average stoichiometry of the alkane, alkene and aromatic hydrocarbon products respectively and  $C_6H_8O_4$  is an indicative formula for the pyrolysis oil.

4 In order to maintain the highest amount of oil product the catalytic pyrolysis process must be carefully controlled to minimise processes such as steam reforming, partial oxidation and auto-thermal reforming (which combines steam reforming and partial oxidation<sup>158,159</sup>) as these reactions lead to H<sub>2</sub>, CO<sub>2</sub> and CO formation.

$$\begin{split} & C_n H_{2n+2} + 2n H_2 O \rightarrow n CO_2 + (3n+1) H_2 & (\text{steam reforming}) \\ & C_n H_{2n+2} + n/2 O \rightarrow n CO + (n+1) H_2 & (\text{partial oxidation}) \end{split}$$

The other important method of controlling product is by careful choice of the catalyst as the chemical nature of the catalyst will define which of the individual reaction steps is most strongly affected. The catalysts used in pyrolysis are described in some detail below.

#### 14.7 Catalysts used in catalytic pyrolysis

The composition and structure of catalysts for catalytic pyrolysis are usually based on either conventional petroleum reforming or cracking catalysts or research materials derived there from. These systems have distinct advantages in terms of scale, availability of supply and cost since they are manufactured on the scale of millions of tonnes per annum. Conventional petroleum catalysts are roughly divided into two classes, alumina-silicates for cracking (i.e. formation of small chain hydrocarbons from long chain hydrocarbons)<sup>160</sup> and transition metal catalysts for reforming (isomerisation and aromatisation).<sup>161</sup> Note that because of the complex nature of these reactions, separating the effects of the catalysts into the simple roles indicated here is overly simplified. The alumina-silicate materials can be divided into several different classes as described below. Petroleum cracking catalysts tend to be alumina or silica supported precious metals or nickel based materials and because of the cost and lifetime of the precious metal catalysts in pyrolysis environments, investigation of these precious metal catalysts is limited to mainly academic work. Cost is an important issue in pyrolysis. Environments are harsh and both poisoning and sintering mitigate against achievement of long catalyst lifetimes. As a possible solution to this low cost materials are of importance and many studies are being carried out in commonly found inorganics such as naturally occurring zeolites (a complex aluminosilicate as described below) and clays. Because of their low cost and plentiful supply, carbonate materials are often used as catalysts in pyrolysis although their use has been largely superseded by the use of aluminosilicate materials. The various types of catalyst are described below. All of these would have a different range in functionality and this should be used to match the various pyrolysis materials used. For example for heavy oils a catalyst with combined cracking, isomerisation and aromatisation catalyst may be used. For a biomass pyrolysis a catalyst with strong de-hydroxylation capability might be preferred. For these reasons, a great deal of research effort is placed in developing the catalysts for a particular raw material as well as the pyrolysis reactor used.

#### 14.7.1 Activated alumina catalysts

For many years it has been known that acid sites are required for catalytic cracking and in the work of Thomas these were thought to be predominantly formed at aluminium sites connected through oxygen ions to silica.<sup>145</sup> These sites are known to promote carbonium ion mechanisms and are probably the major reason for lowering the pyrolysis temperature. Such sites are not present on alumina. However, activated alumina has become an important adsorbent and catalyst and contains both Lewis (electron pair accepting) and Brønsted acid (releases H<sup>+</sup>) sites. It is made by thermal de-hydroxylation of Boehmite, an aluminium oxide hydroxide ( $\gamma$ -AlO(OH)) and yields a highly porous powder of surface area > 200 m<sup>2</sup>/g. The product alumina is normally in the  $\gamma$  or  $\eta$  crystal structure which are conducive to generating high surface areas.<sup>162</sup> The main role of activated alumina catalysts appears to be de-hydroxylation of hydrocarbons.<sup>163</sup> This has been shown for the catalytic pyrolysis of a series of vegetable oils where the products were essentially linear hydrocarbons containing no oxygen.<sup>164</sup> Chang *et al.* have reported that alumina has poor cracking and hydrogenation ability, consequently, the yield of low molecular weight products from wood biomass is small.<sup>136</sup> For a study of the effect of a catalyst on the products of thermal pyrolysis, Samolada *et al.* studied a range of catalysts on the treatment of a synthetic bio-oil.<sup>133</sup> They found that whilst  $\gamma$ -alumina had little cracking ability beyond that expected of thermal treatment it did, however, notably improve the quality of the pyrolysis oil (via de-hydroxylation).  $\alpha$ -alumina (low surface area) used as a catalyst exhibited little of this improvement of the bio-oil material.

#### 14.7.2 Zeolite catalysts

Zeolites are now common catalytic materials in widespread use in the petroleum industry and belong to a wider group of aluminosilicates known as molecular sieves.<sup>165</sup> Zeolites are porous solids with pore sizes around 2–10 Å and are described by IUPAC as microporous. A typical example is shown in Fig. 14.2. Unlike the aluminosilicates that are present in common clays that have a layered structure, zeolites have rigid honeycomb-like pore structures that can survive many reactions (ion-exchange, hydrogenation, hydroxylation and de-hydroxylation)



*14.2* TEM micrograph of a silicate-1 zeolite showing a particle and the parallel pore arrangement (Morris, unpublished data).

without swelling, contraction and collapse of the pore structure. Zeolites are usually hydrated and contain water which is only weakly held. Zeolites are strong solid acids. They are well known for their ion exchange capability which allows the 'doping' of the structure by hetero atoms and, thus, their chemical modification. They are crystalline materials with  $AlO_4$  and  $SiO_4$  units tetrahedrally linked through oxygen anions. In recent times, phosphate groups have been introduced in an effort to generate larger pore systems. Both the atomic and pore structure is periodic and almost 200 zeolite structures have been detailed.<sup>166</sup> Zeolites can be synthesised via hydrothermal condensation of cation precursors in the presence of an organic template<sup>167</sup> but also occur naturally, and the most important natural zeolite is clinoptilolite.<sup>168</sup>

The general catalytic chemistry of zeolites is well reviewed<sup>169</sup> and, in particular, the hydrocarbon cracking properties detailed.<sup>170</sup> Zeolites have high active site densities due to the in balance of anionic charge between the AlO<sub>4</sub> and SiO<sub>4</sub> units.<sup>171</sup> The first found use in petroleum refineries almost 50 years ago where their high activity to hydrocarbon cracking coupled to shape selectivity provided by their pore structure, allowed industrial chemists to achieve greater yields of useful petroleum products.<sup>172</sup> The year 1972 saw the advent of a synthetic high silica zeolite catalyst to the energy industry, HZSM-5, that was able to produce aromatic, petroleum-type products from a wide range of hydrocarbon sources.<sup>173</sup> This material has become the standard against which most pyrolysis catalysts are assessed. The wealth of data available that demonstrates the effectiveness of zeolite catalysts in pyrolysis is now considerable and, therefore, only some of the more recent data is reviewed here.

Zeolites have been widely applied to the catalytic pyrolysis for waste polymer treatments. Despite the advances in polymer recycling for re-use as construction, consumer and retail materials this can be expensive (shipping to low-cost economies for sorting, energy intensive, use of solvents, environmental issues, etc.), result in low-grade products as well as being technically difficult for some polymer types.<sup>174</sup> The opportunity to develop thermolysis methods including pyrolysis (as well as hydrogenation and gasification) for energy generation using waste polymer has been reviewed by Mastellone et al.<sup>175,176</sup> The mechanisms of polymer thermal decomposition are now well accepted.<sup>177</sup> Whilst all aluminium containing zeolites have good cracking capability, it is generally found that the larger pore zeolites such as zeolite-Y (0.74 nm) produce less gas and low molecular weight (hydrocarbons with three to six carbons) products and a higher relative content of aromatics (which increase the product octane number and ensures the smooth running of internal combustion engines and use as a transport fuel<sup>178</sup>) compared to the smaller pore systems such as ZMS-5 (0.55 nm) and zeolite-A (0.4 nm).<sup>41,179–182</sup> The reason for the behaviour is apparently due to the increased number of acid sites on zeolite-Y type systems<sup>183</sup> as well as the small pore size of ZMS-5 which limits the diffusion of larger hydrocarbon moieties during reaction.184

Zeolite catalysts have also been used for the pyrolysis of biomass and related materials. In a study of the pyrolysis of a synthetic bio-oil showed that HZMS-5 was a better catalyst for aromatic production than a range of other zeolite, transition metal and mesoporous catalysts.<sup>133</sup> The catalyst completely removed water and oxygen from the bio-oil in the conditions used but the authors also found that all the catalysts studied increase gas production at the cost of liquid generation. Uzun and Sarioğlu also found that zeolite catalysts decreased liquid yield whilst increasing the proportion of gas and this seems to be a general finding from many studies.<sup>124</sup> As above for polymeric materials, these authors also found that zeolite-Y increased the aromatic content but did maintain the highest liquid yield.<sup>124</sup> Carlson et al. found that ZMS-5 was the catalyst that provided greater aromatic quantise for a range of biomass materials (cellulose, cellobiose, glucose and xylitol) when compared to other zeolites and mesoporous silica.<sup>127</sup> Aho et al. studied a range of zeolite- $\beta$  catalysts over a range of Si:Al ratios of 25–300 and found that the increasing acidity resulted in both greater gas yields as well as the amount of coking.<sup>185</sup> These authors also demonstrated that the catalyst was a prerequisite in generation of polyaromatics from biomass. Zeolite catalysts have been widely used for the catalytic pyrolysis of vegetable and plant oils. One of the first studies of HZSM-5 was for the pyrolysis of corn and peanut oil in 1979.<sup>186</sup> A high aromatic yield was found with the product mixture being akin to a high-grade petrol (gasoline).<sup>186</sup> Similar findings were later reported by Milne and co-workers.<sup>173</sup> It is generally thought that the HZMS-5 catalyst is the most effective type of zeolite catalyst for the conversion of vegetable oils to quality fuel materials.<sup>187,188</sup> Similar effectiveness was found for the conversion of palm oil.189,190

#### 14.7.3 Mesoporous catalysts

Whilst the zeolite catalysts described above are highly effective and form the basis of the majority of large scale process plants (see below for FCC catalysts), scientists are still searching for catalysts to improve the efficiency of catalytic pyrolysis. Probably, the major driving force has been the need to reduce gas yields and, hence, improve liquid content. In order to generate more efficient processes, a further type of molecular sieve materials has begun to be more extensively studied. These are mesoporous materials (normally silicates) that were first detailed by researchers at the Mobil Research and Development Corporation in New Jersey.<sup>191</sup> These are now heavily researched for applications in many fields and readers are referred to a recent excellent collection of papers that provide a comprehensive review of the field.<sup>192</sup> A typical example is shown in Fig. 14.3. The first mesoporous materials were given the abbreviation MCM (Mobil Composition of Matter) and, like zeolites, consisted of tetrahedral silica-oxygen linkages through which ran regularly arranged (periodic), uniform sized pores. Like zeolites, mesoporous materials are formed from organic templating or

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*14.3* Images of mesoporous silica. In this example an hexagonal array of pores are created with two distinct pore sizes. (a) and (c) show images looking through the pore network whilst (b) shows the parallel nature of the pore arrangement. The plot in figure (d) shows the pore size distribution indicating two distinct pore size ranges around 5.5 and 7.5 nm (Morris, unpublished data).

structure-directing molecules but in mesoporous solid synthesis chemistry it is generally thought that the templating species are aggregates of the organics into micellar forms and this results in pore sizes that are around ten times (i.e. in the range of a few nanometre) that of the general zeolitic microporous solids (although much recent work has been carried out to extend this). Where the mesoporous materials differ is that the inorganic framework is amorphous and has no crystalline order and periodicity only arises from the pore structures. The most common pore arrangement is an hexagonal honeycomb arrangement which is more robust than a lamellar and cubic form. Materials that follow the Mobil synthesis route and have the hexagonal structure are normally described as MCM-41 and it is this material (and analogues) that dominates the mesoporous catalytic pyrolysis literature. However, the synthesis chemistry is well-developed and routes to complex combinations of macroporous-mesoporous structures,<sup>193</sup> thin films<sup>194</sup> and complex particle shapes<sup>195</sup> as well as precise control of pore size are well documented.<sup>196</sup>

One of the important steps in providing active mesoporous catalysts is the incorporation of aluminium to provide acid sites and the usual material investigated for catalytic pyrolysis is Al-MCM-41.<sup>197</sup> However, more acidic samples gave greater amounts of coke and gas products suggesting that an optimum aluminium content exists.<sup>197</sup> These authors also report a lack of hydrothermal robustness of these materials and that would have a major effect on the industrial use of these materials.<sup>197</sup> The relative hydrothermal stability of mesoporous silicates compared to zeolites and amorphous aluminosilicates for hydrocarbon cracking is well known.<sup>198</sup> However, they do show good activity for the production of fuel oils from palm oil.<sup>199</sup> Triantafyllidis and co-workers have shown that the nature of the acid site in Al-MCM-41 (since both Brønsted and Lewis acid sites are formed) can have effects on the molecular distribution of the resultant fuel oils.<sup>200</sup> One of the major reasons for the use of large pore systems is the possibility of improving the yield of higher molecular weight products and reducing the gas products. The rationale for the use of mesoporous systems (compared to microporous systems) is that the larger pore systems could allow diffusion and reaction of larger moieties and there is evidence in the MCM system for this pore size effect.<sup>201</sup>

Larger pore mesoporous systems include SBA-15, which is known to be more hydrothermal robust (because of thicker pore walls than MCM-41) and can be readily synthesised with alumina content.<sup>202</sup> Qiang *et al.* have used various SBA-15 catalysts to study pyrolysis of sawdust.<sup>203</sup> As might be expected, it was found that Al-SBA-15 significantly outperformed SBA containing no aluminium analogues and that catalytic activity improved with the amount of aluminium added.<sup>203</sup> Aguado and co-workers have shown that Al-SBA-15 can also be used for the catalytic pyrolysis of polyolefins and shows very promising characteristics.<sup>204</sup> In particular, hydrothermally stabilised SBAs outperformed ZSM-5 and this was attributed directly to the larger pore size which reduced diffusional limitations (as described above). To support the conclusion that SBA-15 may be a better pyrolysis catalyst than MCM-14, Cao *et al.* have shown that SBA-15 measurably improves the product fuel quality compared to MCM type materials.<sup>205</sup>

#### 14.7.4 Fluid catalytic cracking (FCC) catalysts

It is beyond the scope of this chapter to describe commercial FCC catalysts in depth. These types of catalysts are extensively detailed in the following chapter and the reader is referred to the data provided there. In this section we will mainly discuss the application of FCC catalysts that can be used directly in the pyrolysis process rather than upgrading of pyrolysis oils. Whilst many catalysts have shown promise, it has proved important to use robust commercially available catalysts in

the development of catalytic pyrolysis as a commercially viable technology. The FCC process allows for efficient conversion of high-boiling point and highmolecular weight hydrocarbon fractions of crude oil into more valuable petrol fuel grades.<sup>206</sup> Their use has been refined since their introduction in the 1960s (for petroleum refining) to allow for high performance, long-life and re-activation in fluidised bed systems. Scherzer has given an excellent view on the design of these catalysts as applied to zeolite-Y.<sup>207</sup> How these catalysts deactivate through a combination of coking, poisoning and attrition and the deactivation of these catalysts is an area of great interest both industrially and academically.<sup>208</sup> The synthesis of zeolite materials usually provides small particles that can not be readily sintered into larger materials because of their highly crystalline nature and these particles are too fine for commercial applications. The basic design of these commercial catalysts allows development of catalyst particles that can be readily supported in a fluidised bed, and an FCC catalyst usually consists of a mixture of activated alumina (as described earlier), the active zeolite, a binder (normally a silicate) and an inert matrix (a clay or related material; kaolin is often used). The alumina and the binder provide both mechanical and thermal robustness. The inert matrix allows the formation of larger particles (a few micron in diameter) and pellets (less than 100 micron diameter). Careful synthetic processing is required to allow the hydrocarbons access to and from the active phases within these complex systems. Coking is the major problem (deactivating the active sites as well as physically blocking pore systems) and in use the catalysts are continually re-circulated between the reactor (the riser) and the oxidising regeneration chamber.

FCC catalysts have been widely used for catalytic pyrolysis of polymers,<sup>209</sup> biomass<sup>133</sup> as well as various vegetable/plant oils.<sup>210</sup> Samolada et al. found that FCC catalysts were effective in the pyrolysis of a bio-oil producing low coke and gas yields compared to several other zeolite and transition metal catalysts.<sup>133</sup> The catalyst also effected the greatest degree of de-hydrolysis but the stability of the oil was somewhat lower than other catalysts.<sup>133</sup> Ioannidou et al. found that FCC catalysts were effective in the pyrolysis of corn cobs and stalks providing a higher quality biooil than in the absence of catalyst.<sup>27</sup> A similar finding was made by Antonakou and co-workers who found that the use of an FCC catalyst greatly improved the stability of the pyrolysis oil compared to thermal pyrolysis in its absence.<sup>142</sup> Work by Lu et al. reports that FCC catalysts (for pyrolysis of biomass) based on a combination of HZSM-5 and y-Al2O3 are more effective in improving both isomerisation and aromatisation than a zeolite-Y based material.<sup>211</sup> Zhang et al. have recently published excellent work on FCC catalysed pyrolysis of corn cobs.<sup>212</sup> They compared different relative volumes of catalyst and biomass in a fluidised bed and found the ratio had a profound effect on the product distribution. Whilst fresh catalyst resulted in greater dehydration of the corn, used catalyst resulted in greater oil yields. It was also found that the improvement in stability of the product oil was related to the reduction of some active oxygenated hydrocarbon species that promoted polymerisation.<sup>212</sup> The use of FCC catalysts to upgrade bio-oil produced by pyrolysis of lignin through the

removal of polymerisation active phenols has recently been reported by Gayubo *et al.*<sup>213</sup> These results all point to the effectiveness of these catalysts. It should be stressed that the majority of pilot-scale testing of these technologies for biomass pyrolysis has been largely dominated by these catalysts.

FCC type catalysts appear successful for pyrolysis of heavy oils but the amount used has to be carefully controlled in order to optimise the yield of oil and an ideal product distribution.<sup>147</sup> In polyolefin pyrolysis FCC catalysts have been shown to be particularly effective with good production of lighter hydrocarbons and good aromatic content. Indeed, the performance of FCC catalysts appears to be significantly better than zeolite-Y or ZMS-5 with not only improved liquid yields but a greater proportion in the gasoline/petrol composition range.<sup>214</sup> The reason for the more effective behaviour of these catalysts appears to be the bimodal pore size distribution arising from the combination of microporous and mesoporous structures exhibited by the different materials used in the formulation of these materials.<sup>215</sup> One of the more consistent findings for these catalysts for polymer pyrolysis is that spent (i.e. after cycling through the reactor and regenerator in typical FBRs) materials have better than expected or even better performance characteristics than fresh catalysts and this appears to be true for a range of polymers and process conditions.<sup>216,217</sup>

#### 14.7.5 Transition metal catalysts

Transition metals and their oxides have well-known ability to crack hydrocarbons<sup>96,97</sup> due largely to the dissociative chemisorption of organic materials on their surface.<sup>218</sup> They are widely used in the oil industry as hydroprocessing catalysts particularly in the treatment of heavy oil fractions derived from crude oil.<sup>206</sup> Hydroprocessing usually consists of three separate processes; hydrotreating (removal of poisons, etc. from the feedstock notably sulphur), hydrogenation (addition of hydrogen across C-C single, double and triple bonds that can lead to molecular dissociation) and hydrocracking. The ability of metal based catalysts to crack large molecules into smaller ones has led to their use in pyrolysis as gasification catalysts for hydrogen production using water (steam reforming).<sup>219</sup> Iron and nickel based catalysts have been shown to significantly increase the proportion of gas (notably hydrogen).<sup>39</sup> Chromium oxide has also been shown to be highly effective in gasification of sawdust.<sup>29</sup> However, against this background of gasification reactions, some transition metal oxide based catalysts have been used for the production of liquid fuels from biomass. Zinc oxide has been used for the pyrolysis of wood sawdust.<sup>220</sup> Zinc oxide was found to be a rather gentle catalyst that did not completely dehydrolyse the biomass affecting largely sugars and polysaccharides.<sup>220</sup> It did, however, produce stabilised oil.<sup>220</sup> Chang et al. have found that alumina supported CoMo and NiMo catalysts were effective materials for production of petroleum products from wood sources.<sup>136</sup> The CoMo catalyst produced the greatest yield of light aromatics whilst NiMo produced the highest amount of methane.<sup>136</sup> This is as expected since nickel is a more effective cracking catalyst than cobalt. Transition metal catalysts have also been used for the generation of fuel oils from triglycerides (see chapters later in this book). da Rocha Filho *et al.* found that an alumina supported NiMo catalyst could be used to produce alkanes and alkyl benzenes from a number of vegetable oils.<sup>221</sup> Craig and co-workers have similarly shown the effectiveness of transition metals in this area.<sup>222</sup>

#### 14.7.6 Carbonate derived catalysts

The final group of catalysts used in pyrolysis are the carbonates. Their use is based on the availability and low cost of these minerals (e.g. dolomite - $CaMg(CO_2)_2$ ). This ensures that these catalysts are essentially disposable and expensive regeneration processing is not required. Their primary use has been as gasification catalysts rather than as liquid fuel oil generators.<sup>223</sup> For use (the catalysts are pre-calcined to remove carbonate as CO<sub>2</sub>) and in use, the materials are in oxide form and their activity decreases if carbonate is present.<sup>224</sup> Reviews of work can be found under the authorship of Delgado et al.<sup>225</sup> and Sutton et al. <sup>226</sup> Because of the relative inactivity of these catalysts, the process temperatures used are significantly greater than for the catalysts described above. Encinar and co-workers have described the catalytic pyrolysis of olive oil waste over dolomite<sup>135</sup> and their work is fairly representative of many of these studies. The dolomite derived catalysts show great thermal and mechanical robustness and can be used several times with little sign of performance decrease.<sup>135</sup> The yield of hydrogen was seen to increase markedly with temperature (at the cost of a decrease in liquid yield) and amount of catalyst.<sup>135</sup> Sodium carbonate has been successfully used in the catalytic pyrolysis of vegetable oils. There is some debate on the production of aromatics using this catalyst. Konwer et al.<sup>227</sup> and Zaher and Taman<sup>228</sup> suggest that sodium carbonate can yield significant amounts of aromatics from seed oil pyrolysis. These results are somewhat contrary to those of Dandik and Aksoy who found that very little aromatic content was produced.<sup>229</sup>

#### 14.8 Conclusions and future trends

This work sets out a comprehensive review of catalytic pyrolysis centred on the production of fuel oils for use in transportation and energy production. An overview of pyrolysis economics is given and the environmental requirement to generate fuels that are environmentally benign. It should be stressed that catalytic pyrolysis should be viewed as a 'refinement' of thermal pyrolysis. The products of conventional thermal pyrolysis are a bio-oil that can be combusted in turbines and boilers but has less value for transportation because of its stability and quality. Catalytic pyrolysis can be viewed as a technique to upgrade the pyrolysis products to transportation fuel quality. This is important because transport accounts for around 70% of all fossil fuel use. Pyrolysis is a sustainable technology using

waste materials, fast-growing low value crops and other organic materials such as polymers that can only be recycled at considerable cost. It can be almost carbon neutral and through combustion of waste pyrolysis products such as char and gas the process costs can be reduced to effectively zero (since pyrolysis is an endothermic process). Methods and techniques in the general area of pyrolysis are reviewed in order to introduce the technology and science of catalysed pyrolysis. A thorough review of the science of catalytic pyrolysis, the process methodology and the catalyst and feedstocks are provided.

The development of catalytic pyrolysis into a common and widespread commercial technology is reliant on a number of factors. The construction of pyrolysis plants is capital intensive and profitability requires the products to be competitive against fossil fuel prices or to be preferentially marketed with proactive government subsidies. However, it is clear that the increasing cost and shortages of crude oil will necessitate the development of new fuels akin to petrol/gasoline and diesel. It seems likely that the depletion of fossil fuel sources coupled to increased energy demand will ensure the uptake of new and emerging technologies such as pyrolysis. Whilst it is generally accepted that bio-fuels will become an increasingly important component of global energy strategy, there are a number of parallel and competitive technologies for generation of biofuels. Pyrolysis has considerable advantages over some of these competitive techniques such as fermentation and bio-degradation because it is closer to market and is based on well-established and large scale methods used in the petroleum industry. Pyrolysis also offers considerable advantage in that it does not place further pressures on food security as it does not require sugar-rich crops. It should also be noted that catalytic pyrolysis products are a direct replacement for current energy/transportation fuels and do not necessitate any costly technological development of turbines, boilers or internal combustion engines. In many cases and in properly controlled processes, the catalytic pyrolysis products are indistinguishable from conventional petroleum products and can be distributed through existing infrastructure and retailers. This is a major cost advantage over alternative energy sources such as hydrogen. The choice of biofuel technology will also be partly dependent on the local environment and it is likely that pyrolysis will not be a universal solution. For example in a country that has no facilities for cost-effective recycling of waste polymers, pyrolysis may be a very attractive possibility reducing land-fill, transportation and energy costs. Pyrolysis may also be a preferred option if there are large areas of non-arable land where low-value, fast-growing, sustainable energy crops such as *miscanthus* and switch grass can be readily grown and harvested. Further, areas highly dependent on forestry and agriculture where significant amounts of waste are generated may find pyrolysis a useful technology. One further advantage of pyrolysis is that it is highly scalable and plants can be designed and constructed to process tonnes to thousands of tonnes of feedstock per day.

It should not be thought that catalytic pyrolysis is unproven on the commercial scale; it is at an advanced stage of development and, in all likelihood, will become

ever more important. Commercial scale plants operate in China due to a shortage of crude oil and the poor quality of China's oil stocks. The uptake of pyrolysis technology in China has been reviewed.<sup>141</sup> Progress in pyrolysis has been rapid, Envergent Technologies now offers commercial technology to prospective partners.<sup>230</sup> Envergent Technologies is a Honeywell company that combines pyrolysis expertise (Ensyn Corp.) with petroleum refining and process technology from UOP which have been leaders in refining and catalyst technologies for over 100 years. Evergent offers a fast pyrolysis process for biomass (forestry, paper manufacture and agricultural waste materials) via a circulating transported FBR system similar to the one used in conventional petroleum cracking technologies. The production of transportation grade fuels is via a secondary upgrading process using hydroprocessing technology. This technology is expected to be available for licensing of large scale production (2000 tonnes per day) from 2012. In November 2009, Envergent Technologies announced a partnership with the Italian power company Industria e Innovazione for the development of a facility to convert biomass (pine forest residue and waste wood from construction) into pyrolysis oil for renewable power generation. Whilst the planned plant is only of the scale 150 tonnes per day, it represents a major step in commercialising pyrolysis. It thus seems that pyrolysis and catalytic pyrolysis will truly be an emerging technology. Further research and development are required to maximise yields from many sources and provide catalysts of improved efficacy but the technique and methods have been established for both commercial and environmental exploitation.

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**Abstract:** This chapter highlights the feasibility of fluid catalytic cracking (FCC) units for the production of biofuels from different biomass feedstocks. Special attention will be focused on catalytic cracking of triglycerides, which are probably the most suitable feedstocks for their processing in FCC units since they possess density, viscosity and hydrogen/carbon ratio quite similar to those found in vacuum or hydrotreated gasoil usually fed to this refinery conversion unit. Likewise, we will comment on the influence of physicochemical properties of the different biomass feedstocks on the overall refinery facilities upstream FCC unit.

Key words: fluid catalytic cracking, triglycerides, thermal cracking, bio-oils.

#### 15.1 Introduction

One promising alternative for the production of biofuels is the processing of biomass (cellulosic biomass and triglyceride-based biomass) in conventional oil refineries (Huber and Corma, 2007; Lappas *et al.*, 2009). This alternative involves the co-feeding of biomass-derived feedstocks with typical petroleum feedstocks in conventional refining units. This strategy has significant advantages as compared with conventional processes of biofuels production. Petroleum refineries are already built, and hence, the use of existing infrastructure for the production of biofuels would require little capital investment (Huber and Corma, 2007; Holmgren *et al.*, 2007). Moreover, a wide range of biofuels might be obtained, not only in the range of gasoline and diesel but also in the range of kerosene or fuel oil. The European Commission has set a goal that by 2020, 10% of transportation fuels in the European Union (EU) will be from renewable sources. Co-feeding biomass-derived molecules into a petroleum refinery could rapidly decrease our dependence on petroleum feedstocks and allow reaching the target of a more sustainable transport.

Several options are available for converting biomass-derived feedstocks into biofuels in a petroleum refinery: (1) Thermal (visbreaking and cocker units) and catalytic [fluid catalytic cracking (FCC) unit] cracking, (2) hydrotreating and (3) hydrocracking. Hydrogen-based processes are typically more expensive than cracking because they require hydrogen, and this consumption is even higher when biomass feedstocks are processed. Likewise, there are other drawbacks that limit the co-processing of biomass in hydrogen-based units, such as the poisoning of catalysts by water coming from hydrodeoxygenation reactions and the low

quality of the resulting hydrogenated product to be used as diesel (mainly bad cold properties). Both issues require additional conditioning steps, and hence modification of refinery unit. Cracking reactions in a petrol refinery can be carried out in presence of catalyst (FCC unit) and in its absence (thermal units). Thermal units are not considered of interest for the production of biofuels since the resulting organic liquid product (OLP) contains a high content of oxygenated compounds independently of biomass feedstocks, and this reduces its interest as fuel transport. In contrast, catalytic cracking is faster and more selective than thermal cracking that allows working under milder reaction conditions, and hence minimizing yield towards gases, coke and heavy fractions and maximizing the production of liquid fraction suitable for use as transport fuel. Moreover, the presence of the catalyst shows a great ability to remove the oxygen-containing compounds and convert them into CO, CO<sub>2</sub>, H<sub>2</sub>O and a mixture of free oxygen hydrocarbons, although the extent of the oxygen removal is strongly dependent on the features of the initial feedstocks, as will be discussed in this chapter. A simplified reaction pathway for cracking reaction is outlined in Eq. 15.1.

$$C_{x}H_{y}O_{z} \rightarrow a C_{x-b-d-e}H_{y-2c}O_{z-2b-c-d} + b CO_{2} + c H_{2}O + d CO + e C$$
 [15.1]

FCC is the most widely used process for the conversion of crude oil into gasoline and other hydrocarbons because of its flexibility to changing the feedstocks and product demands. The FCC process consists of three main steps: reaction process, separation of the products and regeneration of the spent catalysts. In the first step, a hot particulate catalyst is contacted with hydrocarbon feedstocks in a riser reactor to crack it, thereby producing cracked products and spent coked catalyst. After the cracking reaction takes place, the catalyst is largely deactivated by coke. Thus, at the end of the riser reactor, the spent catalyst is separated from the hydrocarbon products, stripped and sent to a fluidized bed regenerator to burn the coke and reactivate the catalyst. The hot catalyst is then recycled to the riser reactor for additional cracking and products are separated in a distillation column. A variety of process configurations and catalysts have been developed for the FCC process. FCC catalysts usually contain mixtures of a Y zeolite within a silica-alumina matrix, a binder, clay and some additives. Using FCC units for biomass conversion does not require any modification in the catalyst or the process itself. Moreover, the co-processing of renewable feedstocks in the FCC unit might involve some other process benefits such as an increase in the coke production, which could help to maintain the thermal balance between the reactor and the regenerator in the FCC unit; higher olefin production in the gas fraction, which favours the application of these compounds to produce polymers, alkylates and tertiary ethers; an increase in the amount of gasoline and in its octane number due to enhancement of aromatization reactions and olefins production and a decrease in the heavy fractions with a low commercial value obtained usually in the FCC unit.

Renewable feedstocks suitable to be fed in FCC units include highly oxygenated biomass such as bio-oils, glycerol, lignin and sugars, as well as triglycerides with

low oxygen content. Figure 15.1 schematizes the different routes to produce biofuels by means of catalytic cracking. The main challenge of this catalytic process is the removal of oxygen from biomass and enriching the hydrogen content of the final hydrocarbon product in order to improve their fuel properties. Chen *et al.* (1986) have defined the effective hydrogen index, (H/C<sub>eff</sub>), where H, C, O, N and S correspond to the moles of hydrogen, carbon, oxygen, nitrogen and sulphur, respectively, which are present in the feed (Eq. 15.2).

$$(H/C)_{eff} = \frac{H - 2O - 3N - 2S}{C}$$
[15.2]

As seen in Fig. 15.1, this index for highly oxygenated feedstocks is clearly lower than 1, which means that these feedstocks are mainly formed by hydrogendeficient molecules. This index for a mixture of hydrocarbons ranges from 2 (liquid alkanes) to 1 (for benzene). In contrast, triglyceride-based biomass (nonedible vegetable oils and animal fats as well as waste cooking oil) shows hydrogen index of ca. 1.5, which is quite similar to that of a mixture of hydrocarbons. These different values induce distinct chemistry involved in cracking process which will result in different product distribution. Likewise, other physical properties such as viscosity can affect dramatically the catalytic performance in the FCC unit.

Nevertheless, for the co-processing of renewable materials in a refinery, it is also necessary to take into account other important issues upstream FCC unit. The stability of refining streams in the storage, pre-heating or separation devices of a refinery is well known, as well as the compatibility with the materials of the



15.1 Routes to produce biofuels from catalytic cracking processes.

different systems. However, this behaviour is still unknown for biomass feedstocks and their mixtures with petrol feedstocks. Stability problems during their storage might occur as a consequence of low thermal and oxidative stability of renewable raw materials as well as corrosion problems might arise from the presence of free fatty acids. Likewise, stability and corrosion of these mixtures under higher temperature, similar to that found in feed lines and heat exchangers prior to the FCC reactor system, must also be taken into consideration.

# 15.2 Catalytic cracking of highly oxygenated biomass-derived feedstocks

### 15.2.1 Catalytic cracking of bio-oils

Bio-oil is a chemically complex mixture of more than 300 oxygenated compounds, the main constituents being acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols and phenol derivatives, as well as carbohydrates and a large proportion of lignin-derived oligomers. Liquefaction and pyrolysis are the two major technologies to produce bio-oils. Their properties depend on the specific feedstock and conditions of the production process such as temperature, period of heating, ambient conditions and the presence of oxygen, water and other gases. The possible utilization of bio-oil is, however, limited because of some negative attributes such as low pH, low heating value, high oxygen content and high viscosity. Bio-oil component can be converted into more stable fuels using zeolite catalysts (Bridgwater, 1994). Reaction conditions used for the above process are temperatures from 350°C to 500°C, atmospheric pressure and gas hourly space velocities of around 2 h<sup>-1</sup>. The products from this reaction include hydrocarbons (aromatic, aliphatic), water-soluble organics, water, oil-soluble organics, gases (CO<sub>2</sub>, CO, light alkanes) and coke. During this process, a high number of reactions occur, including dehydration, cracking, polymerization, deoxygenation and aromatization. However, poor hydrocarbon yields and high yields of coke generally occur under reaction conditions, limiting the usefulness of zeolite upgrading.

Bakhshi and co-workers studied zeolite upgrading of wood-derived fastpyrolysis bio-oils and observed that between 30 and 40 wt.% of the bio-oil formed coke or char (Adjaye *et al.*, 1996; Katikaneni *et al.*, 1995a; Sharma and Bakhshi, 1993). The ZSM-5 catalyst produced the highest amount (34 wt.% of feed) of OLPs of any catalyst tested. The products in the organic liquid were mostly aromatic for ZSM-5 and aliphatic for SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Gaseous products included  $CO_2$ , CO, light alkanes and light olefins. However, bio-oils are thermally unstable and thermal cracking reactions occur during zeolite upgrading that leads to a high coke formation. Bakhshi and co-workers also developed a two-reactor process, where only thermal reactions occur in the first empty reactor and catalytic reactions occur in the second reactor that contains the catalyst (Srinivas *et al.*, 2000). The advantage of the two-reactor system is that it improves catalyst life by reducing the amount of coke deposited on the catalyst.

The transformation of model bio-oil compounds, including alcohols, phenols, aldehydes, ketones, acids and mixtures, has been studied over HZSM-5 catalysts (Fig. 15.2) (Gayubo et al., 2004a, 2004b, 2005). Alcohols were converted into the corresponding olefins at temperatures around 200°C; then, the olefins obtained were transformed into higher olefins (either butenes or  $C_5^+$  olefins) above 250°C. At temperatures higher than 350°C, the olefins are transformed into  $C_4^+$  paraffins and a small proportion of aromatics. Phenol has a low reactivity on HZSM-5 and only produces small amounts of propylene and butanes. 2-methoxyphenol also has a low reactivity to hydrocarbons and thermally decomposes generating coke (Gayubo et al., 2004a). Acetaldehyde had a low reactivity on ZSM-5 catalysts, and it also underwent thermal decomposition leading to coking problems. Acetone, which is less reactive than alcohols, converts into  $C_5^+$  olefins at temperatures above 350°C. These olefins are then converted into  $C_5^+$  paraffins, aromatics and light alkenes. Acetic acid is first converted to acetone, and that then reacts as above. Products from zeolite upgrading of acetic acid and acetone give considerably more coke than products from alcohol feedstocks (Gayubo et al., 2004b). Therefore, the majority of biomass-derived molecules produce large amounts of coke when passed over acidic zeolite catalysts. Gayubo et al. have recently studied the catalytic transformation of the aqueous fraction of crude biooil obtained via the flash pyrolysis of sawdust (from Pinus insignis) at 450°C over



*15.2* Products from zeolite upgrading (HZSM-5) of model bio-oil compounds including propanol, butanol, acetone, butanone and acetic acid (Gayubo *et al.*, 2004a, 2004b).

HZSM-5 zeolite (Gayubo *et al.*, 2009, 2010). Previously, the bio-oil has been subjected to stabilization treatments to minimize coke deposition on the catalyst and to attenuate deactivation. Co-feeding methanol (around 70 wt.%) minimizes coke deposition within and outside the catalyst particles, thereby increasing the viability of crude bio-oil upgrading (Gayubo *et al.*, 2009). Furthermore, the deposition of coke might also be controlled in a specific step of thermal treatment prior to the catalytic reactor minimizing deposition on the catalyst and thereby attenuating deactivation (Gayubo *et al.*, 2010).

The options for utilizing bio-oils in refineries are affected by its high acid number, high water content, high oxygen content and high metal content, particularly potassium and calcium. Metals can be removed with guard beds or ion exchange. Removal of metals is required before processing because these materials will typically poison catalysts. The low thermal stability, high water content and very high oxygen content make it difficult to blend the bio-oil with common refinery intermediate streams such as vacuum gasoil (VGO). The most serious problem for bio-oil processing is its high acid number that causes corrosion in standard refinery units. The industry standard for refinery vessels is that the total acid number of the blend must be less than 1.5 mg KOH/g. Bio-oil can probably be processed using 317 stainless steel cladding, which is not standard in refinery units. Therefore, bio-oils would require pre-processing in a 317 stainless steel system to reduce the acid number before processing in typical refinery units (Holmgren et al., 2007). Since the FCC is the biggest unit and the heart of most refineries, much more development work would be required to minimize refinery risk before such an approach was viable. As an alternative to blending, co-processing bio-oil with petrol feedstocks in an FCC unit might be possible if a separate feed system was used to inject the bio-oil. Hence, the direct feeding of bio-oils into standard refinery does not appear a straightforward task.

Among various upgrading processes, hydrodeoxygenation is a promising alternative to reduce the acidity and oxygen content. Bio-oil was hydrotreated at high pressures (2000–2500 psi) and low space velocities (0.1–0.2 LHSV) by Holmgren et al. (2007). At these high pressures and low space velocities, hydrodeoxygenation predominates. Large quantities of hydrogen are required to generate water during hydrodeoxygenation because of the high level of oxygen (46%) in bio-oil. The resulting hydrotreated oil was then cracked in an FCC or hydrocracker to produce gasoline. This approach is unlikely to be commercially viable because of the high hydrogen requirement and the high capital cost of the hydrotreatment step. Samolada et al. (1998) reported a two-step process of thermal hydrotreatment and catalytic cracking of biomass flash pyrolysis liquids (BFPLs). Thermal hydrotreatment of BFPLs can be effectively operated, producing liquid products that can be upgraded in a refinery. The heavy liquid product of this process (HBFPL), mixed with light cycle oil (LCO) (15/85 wt./wt.), was considered as a potential FCC feedstock. Commercially available cracking catalysts were found to have an acceptable performance. The obtained bio-gasoline quality is comparable with that of the VGO cracking but with low yields of approximately 20 wt.%. The co-processing of gasoil with a thermally hydrotreated bio-oil has also been investigated by Lappas *et al.* (2009). The results showed that the presence of the bio-oil favours the gasoline and diesel production but increases the coke yield. However, depending on the concentration of biomass liquids, it was shown that this option is technically viable for FCC units running with good quality feedstocks, that is the FCC unit with excess coke burning capacity.

# 15.2.2 Catalytic cracking of other oxygenated feedstocks (lignin, glycerol and sugars)

Lignin, which consists of polyaromatic oxygenated compounds, represents a major fraction of biomass (10-30%) and is currently used as a low-grade fuel to provide heat in the pulp and paper industry, but it would be highly desirable to produce value-added products from lignin. Lignin can be converted into a transportation fuel by dehydroxygenation or zeolite upgrading. These are the same methods used to upgrade bio-oils, which contain a large fraction of lignin-derived products. Thring et al. (2000) studied zeolite upgrading of lignin with HZSM-5 zeolite as a catalyst in a fixed bed reactor operating at an atmospheric pressure, over a temperature range of 500-650°C and weight hourly space velocities of 2.5-7.5/ hour. The liquid product fraction, which consisted of mostly aromatic hydrocarbons (mainly benzene, toluene and xylene – with toluene dominating), was maximized at a temperature of 500°C and a space velocity of 5/hour. On the other hand, the gas product consisted of olefins, light hydrocarbon gases, CO and CO<sub>2</sub> and was produced at the highest yield at a temperature of 650°C and a space velocity of 5/hour. Among the light hydrocarbon gases produced from the lignin, ethylene and propylene were the olefins produced in the highest quantities. Coke and char formation was particularly high at the low reaction temperatures employed in this work but decreased rather drastically with increasing temperature. For instance, at a space velocity of 5/hour, 50 wt.% of the lignin was converted to coke and char when a reaction temperature of 500°C was used compared to only 21 wt.% at 650°C. Small FCC pilot tests were run to determine the crackability of pyrolysis oil and pyrolytic lignin blended with VGO (Holmgren et al., 2007). In the blends, the VGO serves as a hydrogen donor. Compared to VGO, the pyrolysis oil and pyrolytic lignin tend to form high levels of coke. For the blends of VGO with pyrolysis oil or pyrolytic lignin, the acid bio-oils appeared to increase the crackability of the VGO and shift VGO yields towards increased light ends and lower LCO and clarified slurry oil (CSO), which is an economically attractive outcome. Nevertheless, the high levels of coke obtained with both blends (7% and 9%, respectively) would be unacceptable for most FCC units.

Glycerol is produced from biomass through fermentation of sugars and mainly by transesterification of vegetable oils during biodiesel production. The glycerol market is currently undergoing radical changes, driven by very large supplies of glycerol arising from biodiesel production. Glycerol is currently too expensive to be used as a fuel; however, as biodiesel production increases, the price of glycerol will decrease. Corma et al. (2007) studied the catalytic cracking of aqueous glycerol and its mixture with VGO in a microactivity test (MAT) reactor at 500-700°C with six different catalysts. Products from this reaction include olefins (ethylene, propylene and butanes), aromatics, light paraffins (methane, ethane, propane), CO, CO<sub>2</sub>, H<sub>2</sub> and coke. The ZSM-5 catalyst had the highest level of olefins and aromatics and the lowest level of coke (< 20%) in the catalytic cracking of glycerol, whereas the other catalysts had high coke yields (30-50%). When glycerol is fed together with VGO, interactions between the hydrocarbon components and the glycerol reaction intermediates occur, resulting in final selectivities better than those calculated by considering a simple additive effect. These experiments showed that mixtures of VGO with biomass-derived feedstocks can help to transfer hydrogen from the VGO to the biomass molecules. One option for further improving the olefin and aromatic yields for co-feeding of glycerol and petroleum-derived feedstocks into an FCC reactor might involve adding ZSM-5 to the FCC catalyst because ZSM-5 produced more olefins and less coke than FCC catalyst.

Sugars can be used as feedstock for fuels production by different processes. Chen (1976) discussed the conversion of carbohydrate materials to petroleumtype hydrocarbons. The process is composed of microbial conversion of agricultural carbohydrate materials to alcohols followed by direct conversion of the oxygenated microbial reaction product to a hydrocarbon product comprising a substantial highly aromatic fraction. This latter conversion was carried out in the presence of a ZSM-5 zeolite at about 260–540°C. Later, Chen and co-workers (Chen and Koening, 1990; Chen et al., 1986) passed concentrated sugars, including glucose, xylose, starch and sucrose, over ZSM-5 at a temperature from  $300^{\circ}$ C to  $650^{\circ}$ C and observed hydrocarbon, CO, CO<sub>2</sub>, coke and water as products. The addition of methanol to the feed decreased the amount of coke and increased the hydrocarbon products. The hydrocarbon products consisted of gaseous alkanes (methane, ethane, propane), liquid alkenes and alkanes (butane, pentene, hexane) and aromatics (benzene, toluene,  $C_8-C_{10}$  aromatics). One of the problems of this reaction is that when methanol is not used, 40-65% of the carbon is converted into coke.

### 15.3 Catalytic cracking of triglyceride-based feedstocks

The high molecular weight and size of triglycerides molecules, which comprise vegetable oils and animal fats, prevent their direct use as transport fuels, and hence, they must be upgraded. Hydrotreatment of triglyceride-based feedstocks (vegetable oils and animal fats) for automotive fuels has been studied in detail (Bezergianni *et al.*, 2009; Huber *et al.*, 2007; Lappas *et al.*, 2009; Petri and Marker,

2006). Hydrocracking of these renewable raw materials has been also studied by several authors (Bezergianni *et al.*, 2009; da Rocha Filho *et al.*, 1993; Gusmão *et al.*, 1989; Kubicková *et al.*, 2005). However, high amounts of hydrogen are required to enhance hydrodeoxygenation processes. Such reaction pathway implies the conversion of the oxygen present in the triglyceride in form of water (Gusmão *et al.*, 1989; Huber *et al.*, 2007). The formed water, as well as the initial content in the feedstocks of metals (such as sodium, potassium, calcium or phosphorous), and other impurities (solid particles, water or detergents) are associated with problems related to the durability of the sensitive hydrogenation catalyst (Petri and Marker, 2006). Furthermore, there is always a problem with the operating costs related to the high hydrogen consumed along the reactions, which advise against the co-processing of renewable raw materials in refining units that work with high-pressured hydrogen.

On the other hand, there is the possibility of cracking triglyceride-based feedstocks in refining units without the presence of hydrogen. These possible units are thermal cracking units such as visbreaker or coker and the FCC unit. Thermal cracking units are used for the breakdown of heavy crude oil into smaller molecules in the absence of catalyst and hydrogen. Several vegetable oils have been thermally cracked and the results reported in literature: tung oil (Chang and Wan, 1947), soybean oil (Demirbas and Kara, 2006; Lima et al., 2004; Schwab et al., 1988), high-oleic safflower oil (Schwab et al., 1988), palm oil (PO) (Chew and Bhatia, 2008; Lima et al., 2004), castor oil (Lima et al., 2004), canola oil (Idem et al., 1996; Sadrameli and Green, 2007), several tropical vegetable oils (Alencar et al., 1983) and oleaginous waste feedstocks such as waste cooking oil (Dandik and Aksoy, 1998), oils from non-edible fruits (such as Macauba fruit; Fortes and Baugh, 1999, 2004) and non-edible animal fats (Adebanjo et al., 2005; Demirbas, 2009). Moreover, Padmaja et al. (2009) have recently reported the thermal cracking of a biocrude extracted from Calotropis procera (laticiferous arid plant from India) under conditions similar to those found in visbreaking and delayed coking. All of the above-mentioned reactions have been usually performed in batch reactors, although fixed bed reactors (usually under the presence of inert materials) and fluidized bed have been also reported. Temperature ranges usually between 300°C and 500°C and the operating pressure is always close to the atmospheric. From this work, a high amount of oxygenated hydrocarbons is found in the final reaction products independently of reaction temperature. Although the thermal decomposition of triglyceride molecules and their associated heavy oxygenated hydrocarbons is always initiated at temperatures of 240-300°C (without the presence of oxygen) (Adebanjo et al., 2005; Crossley et al., 1962), the presence of a catalyst is necessary to remove oxygen from oxygenated hydrocarbons such as carboxylic acids, esters, aldehydes or ketenes and to obtain an organic liquid fraction suitable for gasoline and diesel formulation. Thus, the co-feeding of this renewable feedstock to an FCC unit would be more feasible. This unit is the most widely used process for the conversion of heavy fraction of crude oil into high-value products (e.g. diesel, gasoline). This unit operates under high temperatures (>  $500^{\circ}$ C) and pressure close to the atmospheric in the absence of hydrogen and the presence of an acid catalyst.

In this section, we will discuss the chemistry involved in the catalytic cracking of triglyceride molecules as well as the work dealing with the processing of this biomass feedstock under FCC realistic conditions.

### 15.3.1 Catalytic cracking of triglycerides molecules over acid catalysts: general reaction pathway

First studies dealing with the catalytic cracking of triglycerides molecules date from 1979 over ZSM-5 catalyst (Weisz *et al.*, 1979). In this pioneering work, the authors performed the catalytic cracking of several vegetable oils achieving complete conversions of them in a mixture of paraffinic, olefinic and, above all, aromatic hydrocarbons (ca. 42–78%). After this initial work, a huge amount of work dealing with this topic has been reported in the literature over different acid catalysts: zeolitic molecular sieves (such as HZSM-5, H-Y and H-mordenite) (Bhatia *et al.*, 1998; Idem *et al.*, 1997; Katikaneni *et al.*, 1995b, 1995c, 1996; Leng *et al.*, 1999; Milne *et al.*, 1990; Ooi *et al.*, 2005; Prasad and Bakhshi, 1985; Prasad *et al.*, 1986a, 1986b; Twaiq *et al.*, 1999), Al-containing mesostructured materials (Al-MCM-41 and Al-SBA-15) (Bhatia *et al.*, 2009; Demirbas, 2009; Idem *et al.*, 1997; Ooi and Bhatia, 2007; Ooi *et al.*, 2004, 2005; Twaiq *et al.*, 2003a, 2003b) and amorphous materials (alumino-silicates, pillared clays and alumina) (Boocock *et al.*, 1992; Katikaneni *et al.*, 1995b, 1995c; Idem *et al.*, 1997; Vonghia *et al.*, 1995).

Products usually obtained by means of the catalytic cracking of vegetable oils and animal fats are depicted in Fig. 15.3. They are usually grouped in an 'organic liquid product' (gasoline, kerosene and diesel fractions), gaseous products (hydrocarbons  $C_1-C_5$ , CO, CO<sub>2</sub>), water and coke. The oxygen initially present in the feedstock is removed as water (which is easily isolated), CO and CO<sub>2</sub>. Therefore, there is not a remarkable presence of oxygenated hydrocarbons in the final organic cracking products.

The catalyst properties (e.g. crystalline nature, shape selective effect), the reaction conditions (temperature, pressure, space velocity, presence of steam, type of reactor . . .) and the nature of feedstocks, dramatically influence the conversion and yield towards the different reaction products. Generally, the presence of zeolites increases the yields towards the OLP fraction, whereas amorphous catalysts predominantly produce high amount of gases (Idem *et al.*, 1997; Katikaneni *et al.*, 1995c). Co-feeding steam during the reaction process helps to increase both the olefinic compounds formation and the durability of the catalyst. This fact takes place because the presence of steam diminishes the coke formation and thus the catalyst deactivation (Katikaneni *et al.*, 1995b). The use of a fluidized bed instead a fixed bed reduces generally the selectivity towards the OLP fraction



*15.3* Simplified scheme of products coming from the catalytic cracking of triglyceride molecules over an acid catalyst.

due to the shorter contact time that diminishes the possibility of forming liquid hydrocarbons from the olefins C2-C5 oligomerization reactions (Katikaneni et al., 1997). In all the different studies, an OLP with a high concentration of aromatics has been obtained (over 50%) as well as a high triglyceride conversion (> 80%). Furthermore, the almost null presence of oxygenated hydrocarbons in the final cracking products is confirmed by the different performed studies (Katikaneni et al., 1995c, 1997; Leng et al., 1999; Twaig et al., 2003a). The different authors have shown that although the initial decomposition of triglyceride molecule is mainly a thermal process, in the subsequent secondary cracking reactions (hydrogen transfer, isomerization, oligomerization,  $\beta$ -scission, aromatization), the acid catalyst has a crucial role (Twaiq et al., 2003a). Table 15.1 summarizes the most relevant work dealing with the catalytic cracking of triglyceride molecules indicating type of feedstock, reaction conditions and catalyst. As observed, most of the studies have been performed in fixed bed reactors, in a range of temperatures generally between 300 and 500°C and with liquid space velocities ranging from 2 to 4/hour.

The general reaction pathway of the acid-catalyzed cracking of a triglyceride molecule is depicted in Fig. 15.4. Once the triglyceride molecule has been primarily decomposed to heavy oxygenated hydrocarbons such as fatty acids, ketones, aldehydes and esters, their reactions to reach other products start by means of the breaking of the C–O and C–C bonds by  $\beta$ -scission reactions. The breaking of the bonds C–O and C–C follows two competitive routes: (1)

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Reference	Feedstock	Type of reactor	Reaction conditions	Catalyst
Bhatia <i>et al.</i> (2009)	Palm oil	Fixed bed	Atmospheric pressure, T = 450°C, WVSH: 2.5/h	HZSM-5/alumina, Al-MCM-41/ alumina
Boocock <i>et al.</i> (1992)	Rapeseed oil, coconut oil, triglycerides	Fixed bed	Atmospheric pressure, T = 450°C, WVSH: 0.6–2.11/h	Activated alumina
Chew <i>et al.</i> (2009)	Crude palm oil, used palm oil	Riser reactor	Atmospheric pressure, T = 450°C, C/O = 5 g/g, Residence time = 20 s	Re-Y, HZSM-5, SBA-15, AI-SBA-15
Dandik <i>et al.</i> (1998)	Used sunflower oil	Fixed bed	Atmospheric pressure, T = 400–420°C, Feedstock: 100 g, Residence time = 3 h	HZSM-5
Haag <i>et al.</i> (1980)	Corn oil, castor oil, jojoba seed oil, hydrocarbon-like plant materials	Fixed bed Fluidized bed	Atmospheric pressure, T = 400–500°C, WVSH: 0.5–2.5/h	HZSM-5
ldem <i>et al.</i> (1997)	Rapeseed oil	Fixed bed	Atmospheric pressure, T = 400–500°C, WVSH: 3.2, 12, 15.4/h	Silicalite, silica, Silica-alumina, Gamma-alumina
Katikaneni <i>et al.</i> (1995b)	Rapeseed oil	Fixed bed	Atmospheric pressure, T = 375–500°C, WVSH: 1.8–3.6/h	HZSM-5, H-mordenite, H-Y, silicalite
Katikaneni <i>et al.</i> (1997)	Rapeseed oil	Fluidized bed	Atmospheric pressure, T = 400–500°C, Catalyst: 10 g, Q <sub>Feed</sub> = 175–225 ml/h	HZSM-5
Leng <i>et al.</i> (1999)	Palm oil	Fixed bed	Atmospheric pressure, T = 360–420°C, WVSH: 2–4/h	HZSM-5

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(Continued)

Table 15.1 Continued				
Reference	Feedstock	Type of reactor	Reaction conditions	Catalyst
Ooi <i>et al.</i> (2004)	Fatty acids from palm oil	Fixed bed	Atmospheric pressure, T = 400–450°C, WVSH: 2.5–4.5/h	HZSM-5, MCM-41
Ooi <i>et al.</i> (2005)	Palm oil	Fixed bed	Atmospheric pressure, $T = 450^{\circ}$ C, WVSH: 2.5/h	HZSM-5, MCM-41, SBA-15
Prasad <i>et al.</i> (1986a)	Rapeseed oil	Fixed bed	Atmospheric pressure, T = $340-400^{\circ}$ C, WVSH: $2-4/h$	HZSM-5
Prasad <i>et al.</i> (1986b)	Rapeseed oil	Fixed bed	Atmospheric pressure, T = 340–400°C, WVSH: 2–4/h	HZSM-5
Twaiq <i>et al.</i> (1999)	Palm oil	Fixed bed	Atmospheric pressure, T = 350–400°C, WVSH: 1–4/h	HZSM-5, beta, USY
Twaiq <i>et al.</i> (2003b)	Palm oil	Fixed bed	Atmospheric pressure, $T = 450^{\circ}$ C, WVSH: 2.5/h	AI-MCM-41
Weisz <i>et al.</i> (1979)	Corn oil, peanut oil	Fixed bed	Atmospheric pressure, T = 400–500°C, $\Omega_{Feed}$ = 2 ml/h	HZSM-5

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*15.4* General reaction mechanism for the catalytic cracking of triglyceride molecules over acid catalysts.

decarboxylation (CO<sub>2</sub>) and decarbonylation (CO) reactions followed by C–C bond cleavage of the resulting hydrocarbon radicals or (2) C–C bond cleavage within the hydrocarbon section of the oxygenated hydrocarbon molecule followed by decarboxylation and decarbonylation of the resulting short-chain molecule (Idem *et al.*, 1996). The occurrence of these different reaction routes depends on the double bonds in the initial oxygenated hydrocarbon. Whereas C–C bond breaking in the  $\alpha$  and  $\beta$  positions is favoured in the presence of unsaturated hydrocarbon molecules, decarboxylation and decarbonylation reactions take place before C–C bond cleavage for saturated oxygenated hydrocarbons because, in a saturated hydrocarbon chain, the less endothermic bonding is the one associated with the  $\beta$  position of the carbonyl group (Osmont *et al.*, 2007). Different subsequent cracking reactions finally yield CO, CO<sub>2</sub> and water, as the main oxygenated compounds, and a mixture of hydrocarbons produced by different reactions such as  $\beta$ -scission, hydrogen transfer, isomerization, cyclization

or aromatization, some of them possible because there is an acid catalyst present in the reaction system. Furthermore, coke is formed by means of polymerization reactions (Maher and Bressler, 2007).

# 15.4 Co-processing of triglycerides and petrol feedstocks mixtures in fluid catalytic cracking refinery units

The presence of an FCC catalyst solves the problems related to the thermal cracking of vegetable oils and animal fats. FCC catalysts are very effective in removing oxygen from biomass by transformation into CO<sub>2</sub>, CO and water without using hydrogen and allowing the control of the final product distribution. Thus, as mentioned above, the FCC unit of a refinery seems to be the most appropriate system for the co-processing of this renewable raw material. Moreover, physical properties of triglyceride-based feedstocks are close to those found in typical refining streams that are usually fed to the FCC unit (H/C mass ratio, density, viscosity . . .) as well as the fact of the high miscibility. Co-processing of triglyceride-based biomass in the FCC unit not only would help to achieve the bio-component target fixed by the EU directive (Commission Directive 2009/28/ EC) but also to the improvement of some properties in the final FCC products. Processing these renewable materials in a refinery would lead to a lower content in metals (such as nickel or vanadium) and heteroatoms (such as sulphur or nitrogen) in the final products due to the fact that this feedstock does not contain those metals and heteroatoms in their composition. Moreover, they are formed by paraffinic and olefinic hydrocarbons, more crackable than the aromatic compounds present in the typical streams usually fed to the FCC unit, which tend to remain as unaltered compounds in the low-value heaviest fractions. Other benefits would be a slight increase in the coke production, which could help to maintain the thermal balance between the reactor and the regenerator in the FCC unit; higher olefin production in the gas fraction, which favours the application of these compounds to produce polymers, alkylates and tertiary ethers; and an increase in the amount of gasoline and in its octane number due to enhancement of aromatization reactions and olefins production.

# 15.4.1 Storage stability and corrosion studies of triglyceride and petrol feedstocks mixtures

Considering all the above-mentioned statements, making biofuels through biofeedstocks refining can be an appealing alternative. However, the co-processing of triglyceride-based biomass in a refinery is necessary to enforce several previous studies. The stability of refining streams in the units and conditions of a refinery are well known, as well as the compatibility with the materials of the different systems. Nevertheless, this behaviour is unknown with pure vegetable oils or animal fats streams and their mixtures with petrol feedstocks. Stability problems during their storage might occur as a consequence of their low thermal and oxidative stability, and corrosion might arise from the free fatty acids that contain vegetable and residual oils and animal fats. Storage conditions can lead to density, viscosity or acidity changes, which might affect the processing of renewable materials (vegetable oils and animal fats) in the FCC unit (Geller et al., 2007). For example, in the FCC unit, viscosity of the sample is very important to control its vaporization. Likewise, potential polymers formed under storage conditions of vegetable oils and animal fats could lead to the deposition of gums in the tubes of the heat exchangers and the transfer lines prior to the FCC unit. Moreover, although acidity of vegetable oils or animal fats has a different origin compared to the acidity of oil products (the first one is referred to free fatty acids and the second one to naphtenic acids), acid limitation for refining streams (1.5 mg KOH/g approximately) (Humphries and Sorell, 1976; Piehl, 1988) might be a problem if free fatty acids cause corrosion. Corrosion problems associated with the mentioned free fatty acids of oils and fats are not important in the reaction section of a refinery unit, as the acids react rapidly because of the high temperatures reached. However, it cannot be said the same with the parts of the unit upstream the reactor as storage system where free fatty acids are intact. However, these issues have been poorly addressed in the literature.

We have recently studied the storage stability and corrosivity of a petrol feedstock and renewable materials mixtures under high temperature similar to that found in feed lines and heat exchangers prior to the FCC reactor (Melero et al., 2010a). Precisely, a low-saturated vegetable oil (soybean oil), a highly saturated vegetable oil (PO), animal fat unfit for human consumption and waste cooking oil were selected, whereas vacuum gasoil, hydrotreated vacuum gasoil and atmospheric residue were taken as petrol feedstocks. Storage stability studies were performed by means of an accelerated oxidation process in the presence of oxygen at 140°C according to the UOP 174-84 method (UOP, 1984). Physical properties as well as distillation curve of the samples studied were statistically unchanged after oxidation treatment. Likewise, water and/or sediment content in the samples were not evidenced after thermal treatment. Hence, according to the UOP 174-84 method, the different mixtures can be considered stable in storage at 77°C for periods of at least 180 days. Corrosion studies were also carried out following the UOP 174-84 method slightly modified by the presence of a carbon metal probe ASTM A 293 Gr C. The leaching of metallic species was monitored after thermal treatment. The results showed a negligible leaching of metallic species for pure petrol samples as well as for their mixtures with renewable materials. Hence, this preliminary study opens up good perspectives for the co-processing of triglyceride biomass feedstocks in the existing infrastructure of petroleum refineries, although further studies must be performed in the future.

15.4.2 Catalytic cracking of triglycerides molecules under FCC conditions: product distribution

Although the cracking of vegetable oils into liquid fuels has been studied in detail, the cracking of triglycerides molecules under realistic FCC conditions is less described in the literature. However, certain number of authors have performed studies about the processing of vegetable oils (Bhatia *et al.*, 2007, 2009; Chew and Bhatia, 2009; Dupain *et al.*, 2007; Li *et al.*, 2009; Melero *et al.*, 2010b; Tamunaidu and Bhatia, 2007; Tian *et al.*, 2008) and animal fats (Lummus, 1988; Melero *et al.*, 2010b; Tamunaidu and Bhatia, 2007; Tian *et al.*, 2007; Tian *et al.*, 2008) under conditions that try to simulate operating conditions of the FCC unit. In these studies, the reaction system employed is usually based in a riser reactor and an FCC catalyst. After the catalytic cracking reactions, conversion is usually over 75% (Bhatia *et al.*, 1998; Chew and Bhatia, 2009; Melero *et al.*, 2010b; Tian *et al.*, 2008). Furthermore, there are no remarkable amounts of oxygenated hydrocarbons in the final cracking products, as almost all the oxygen initially present in the triglyceride molecule ends forming water or carboxylic gases (CO and CO<sub>2</sub>) (Dupain *et al.*, 2007; Melero *et al.*, 2010b; Tian *et al.*, 2008).

Figure 15.5 shows the yields towards different products for the catalytic cracking of crude PO in a fixed bed reactor of short contact time at 565°C and a catalyst-to-PO mass ratio of 4 (Melero et al., 2010b). Besides the oxygenated compounds detected (water and carboxylic gases), main hydrocarbon products are gaseous hydrocarbon products, such as dry gas (H<sub>2</sub>, methane, ethane, ethylene) and liquid petroleum gases (LPG, propane, propylene, butenes, butanes), and liquid hydrocarbon products such as gasoline (GLN; C<sub>5</sub>, 221°C), which is divided into light naphtha (LN; C5, 90°C), medium naphtha (MN; 90-140°C) and heavy naphtha (HN; 140–221°C), LCO (221–360°C) and decanted oil (DO; > 360°C). As observed in Fig. 15.5, water is the main oxygenated compound in the cracking of vegetable oils because it involves approximately 70% of the initial oxygen in the triglyceride molecule, which means a yield of water in the final product cracking of ca. 10% when a 100% crude PO feedstock is processed. Similar results have been described in the catalytic cracking experiments performed by different authors (Dupain et al., 2007; Marker, 2007; Ramakrishan, 2004). Water is produced by means of decarboxylation reactions (Idem et al., 1996) as well as catalytic dehydration reactions (Chang and Silvestri, 1977) or condensation processes (Adjaye and Bakhshi, 1995). Carboxylic gases are also important oxygenated compounds with a yield of ca. 5%. Carboxylic gases are formed by CO in 60% mass percentage and CO<sub>2</sub> in 40% (Melero et al., 2010b). CO is formed through decarbonylation reactions from different molecules such as ketenes, aldehydes, fatty acids and esters. By-products of this reaction depend on the original oxygenated compound. On the one hand, in the case of ketenes and aldehydes, decarbonylation reactions lead to reactive species such as free radicals and, on the other hand, in the case of fatty acids and esters, they produce alcohols



*15.5* (a) Product yields and (b) hydrocarbon composition in LPG effluent for the catalytic cracking of crude palm oil under FCC conditions (Melero *et al.*, 2010b).

(Idem *et al.*, 1996).  $CO_2$  is formed through fatty acid and ester decarboxylation reactions, producing water and ketenes as by-products (ketene usually loses its oxygen molecule because of molecular decarbonylation reactions to form ethylene). These data mean that around 17% of the initial oxygen ends as CO and 11% as  $CO_2$ . Hence, 15% of the renewable raw materials that are being fed to the FCC reactor end up as non-valuable products (water and carboxylic gases) under the tested reaction conditions used in this work (Melero *et al.*, 2010b).

Dry gas is mainly a thermal cracking product, although it can be obtained by means of catalytic reactions, especially in the case of ethylene. Dry gas is not an important cracking product because it is obtained in a small percentage (never higher than 5%) and it has a low commercial value. Ethylene is the main compound, leading to more than 40% of the final dry gas yield, and ethane and methane production is always close to 30% for both compounds. On the other hand, LPG production in the case of PO cracking is a very important fraction with a yield of ca. 25% under the tested reaction conditions (Melero et al., 2010b). High yields of gaseous products have also been achieved by other authors working under the FCC conditions (see Table 15.2). Tamunaidu and Bhatia (2007) achieved yields of gaseous hydrocarbons ranging between 19.9% and 38.1% in the cracking experiments of PO using a riser reactor (temperature =  $400-500^{\circ}$ C and catalyst-to-oil mass ratio ranging from 5 to 10). Similar experiments were performed by the research group of Chew and Bhatia (2009). These authors obtained yields of gaseous products of 16.2% and 15.9% for crude and used PO, respectively, using a riser reactor at 450°C and a catalyst-to-oil mass ratio of 5. Finally, Li et al. (2009) confirmed these results, reaching yields to gas of 28.8% in their cracking experiments of cottonseed oil in a fluidized bed reactor (temperature =  $400-500^{\circ}$ C and catalyst-to-oil mass ratio of 6-10).

LPG gases are mainly a catalytic cracking product obtained through dealkylation reactions, in which the hydrocarbon chain bonded to an aromatic ring can be broken to end up as gases (Dupain *et al.*, 2007), or through the initial cracking of higher molecular weight products. LPG hydrocarbons are usually produced by means of  $\beta$ -scission reactions in which a primary carbenium ion and an olefin are formed. Afterwards, it is quite probable that hydride transfer reactions will be produced, transferring the charge from a small carbenium ion onto a large hydrocarbon and, as a consequence, forming new olefins, which can be protonated again by a Brönsted acid site and cracked further or isomerized. Obviously, after hydrogen transfer reactions, paraffins are produced. However, LPG composition is mainly olefinic and much based on propylene (more than 35% of the total LPG), although there are also important amounts of isobutane and, in a less relevant amount, C4 olefins, which are produced in the same quantity between them (Melero *et al.*, 2010b).

The liquid product of a catalytic cracking process is usually composed of cyclic and linear aliphatic hydrocarbons as well as aromatic compounds. The main hydrocarbon liquids considered are GLN, LCO and DO (Melero *et al.*, 2010b; Tian *et al.*, 2008). DO is the heaviest reaction product and, in the case of the renewable raw materials, it is obtained by means of condensation or polymerization reactions (Horne and Williams, 1996; Idem *et al.*, 1996). This fact explains the low yield towards DO of around 2–4.5%, as shown in Fig. 15.5 and Table 15.2, in the results obtained by the research groups of Melero *et al.* (2010b) and Tian *et al.* (2008). On the other hand, GLN is the main liquid compound, with a yield that can be close to 40% of the total product distribution (that means more than 75% of the OLP) (Melero *et al.*, 2010b). The LCO presence is less important, and it implies a yield of ca. 10–15% (Melero *et al.*, 2010b; Tian *et al.*, 2008). Both

Table 15.2 Product yi	ields in the catalytic cracking of t	riglyceride-based feed	stock under	FCC condi	tions			
Research group	Experimental conditions	Feedstock	Product (v	vt.%)				
					OLP			
			Gases		GLN		CO	
Tamunaidu and Bhatia (2007)	Riser reactor T = 400-500°C Catalyst-to-oil ratio = 5–10	Palm oil	19.9–38.1		49.5–59.1	0	0.1–10.4	
Chew <i>et al.</i> (2009)	Riser reactor T = 450°C Catalyst-to-oil ratio = 5	Crude palm oil Used palm oil	16.2 15.9		43.5 33.0	4 4	1.2 1.5	
Li <i>et al.</i> (2009)	Fluidized bed T = 400-500°C Catalyst-to-oil ratio = 6–10	Cottonseed oil	7.5–28.8		25.1–33.7	4	19.5-64.0	
			Gases		OLP			
			Dry gas	БЧЛ	GLN	ГСО	DO	Coke
Tian <i>et al.</i> (2008)	Riser reactor T = 400–500°C Catalyst-to-oil ratio = 6–10	Chicken fat Palm oil Soybean oil	4.48 6.35 4.59	34.34 41.56 29.24	32.75 28.14 32.27	11.40 8.90 15.28	2.95 1.97 4.50	2.31 2.20 3.98

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gasoline and LCO are involved in  $\beta$ -scission, isomerization and hydrogen transfer reactions of the hydrocarbons, which come from decomposition of heavy hydrocarbons. Furthermore, cracking under FCC conditions involves high contents in aromatic hydrocarbons in the organic liquid phase. The high number of dehydrogenation reactions to remove oxygen in the form of water leads to an increase in the olefins formation, which leads to the aromatic compounds formation under the FCC reaction conditions. Concretely, an aromatic content of 30–40% has been reported in the gasoline fraction (Melero *et al.*, 2010b; Tian *et al.*, 2008).

Last reaction product is coke, which is mainly produced by a thermal pathway. Most catalyst deactivation associated with coke formation is produced in the initial reaction period because some of the free radicals formed by thermal processes are not able to go within the catalyst pores and are deposited in the most external part of it (Dupain *et al.*, 2006). Coke can also be obtained from thermal direct polycondensation of either triglyceride molecules or primary heavy oxygenated hydrocarbons (Katikaneni *et al.*, 1997). Furthermore, coke might also be obtained by a catalytic route that involves the formation of polyaromatic compounds coming from a successive hydrogen elimination of aromatic molecules. Nevertheless, coke coming from a catalytic route is always lower than that obtained thermally.

# 15.4.3 Catalytic cracking of triglycerides and petrol feedstocks mixtures under FCC conditions

Several research centres, universities and companies have been working for years in the co-processing of renewable raw materials in FCC refining units. In the studies performed by these authors, it has been shown the technical viability of the co-processing of vegetable oils (palm, rapeseed, soybean or sunflower oils), waste cooking oil and animal fats and vacuum gasoil under FCC conditions (Bormann and Tilgner, 1994; Bormann *et al.*, 1993; Buchsbaum *et al.*, 2004; Carlos de Medeiros *et al.*, 1985; Pinho *et al.*, 2007). Not only the operation conditions registered but also the final products obtained after the catalytic cracking reactions are perfectly compatible with the conditions and products usually related to the FCC unit. However, there is a strong effect of the feedstock composition on the cracking products distribution.

Figure 15.6 illustrates the results of the co-processing of pure PO blended with vacuum gasoil in FCC conditions (Melero *et al.*, 2010b). Data clearly show that the production of all gases (dry gas and LPG) is enhanced by the increase of the non-petrol feedstock in the feed. This fact comes from the presence of triglyceride molecules in the initial feedstock, which reduce the concentration of aromatic rings, which tend to be refractory and more difficult to be cracked. However, comparing the results obtained in the experiments performed by different authors, there is an important difference in the olefin gases production. In some studies (Bormann *et al.*, 1993; Couch, 2007; Ramakrishan, 2004), it is claimed that the



*15.6* Products yields for catalytic cracking of feedstocks with different content in palm oil. Reaction temperature of 565°C and a catalyst-to-oil ratio of 4 g catalyst/g oil. (a) Palm oil/VGO (wt.%) 0/100, (b) Palm oil/VGO (wt.%) 30/70, (c) Palm oil/VGO (wt.%) 100/0 (Melero *et al.*, 2010b).

presence of vegetable oils in the feedstock may enhance the olefins production in comparison with a petrol feedstock, and even UOP has patented a process for the production of olefins  $C_2-C_5$  from renewable raw materials in FCC conditions (Marker, 2007). In contrast, in the work reported by Melero *et al.* (2010b), the olefinity of LPG is not enhanced by the presence of renewable raw materials in the feedstock, and in the case of the VGO, cracking is even slightly higher (see Table 15.3). Nevertheless, these data are in fair agreement with the increase of aromatic compounds in the liquid effluent as the vegetable oil content increases in the feed stream (see data in Table 15.3). The removal of hydrogen from the hydrocarbon molecules to form water under reaction conditions (high temperature, low pressure and high residence time) yielding olefinic hydrocarbons will suffer subsequent cyclization and hydrogen transfer reactions to form aromatic compounds (Dupain *et al.*, 2007; Melero *et al.*, 2010b).

As observed in Fig. 15.6, the increasing content of triglyceride-based biomass in the feed gradually diminishes the yields towards liquids, this effect being more relevant for LCO and DO fractions as compared with GLN (Melero *et al.*, 2010b). Similar conclusions have been achieved by Bormann *et al.* (1993). These results are associated with the higher crackability of vegetable oils and animal fats in comparison with the petrol feedstocks. Hence, the gasoline content in the OLP is always enhanced as the percentage of vegetable oil is increased in the initial feedstock (Bormann *et al.*, 1993; Carlos de Medeiros *et al.*, 1985). For example,

Table 15.3 Olefinity of LPG, naphtha distribution in GLN and aromatic content and distribution in the liquid effluent obtained by the catalytic cracking of feedstocks with different contents in palm oil (reaction temperature of 565°C and catalysts-to-oil ratio of  $4g_{catalyst}/g_{oil}$ )

	Palm oil/VGO (wt.%)		
	0/100	30/70	100/0
Olefinity of LPG			
$C_3 = /C_3 TOTAL$	0.83	0.80	0.80
$n-C_{4}=/C_{4}=0$	0.46	0.45	0.46
$i-C_4^{-2}/C_{4 \text{ TOTAL}}$	0.15	0.13	0.12
Naphtha distribution in GLN (wt.%)			
LN (C5–90°C)	40.36	43.71	51.88
MN (90–140°C)	21.36	18.97	16.65
HN (140–221°C)	38.28	37.32	31.47
Aromatic content (wt.%)			
Monoaromatics	26.98	29.41	36.64
Diaromatics	18.61	20.16	22.54
Polyaromatics	16.72	16.06	11.73
Total	62.31	65.63	70.91

Source: Melero et al. (2010b).

Bormann *et al.* (1993) indicate that the percentage of gasoline in the liquid products rises from 60.3% to 61.1%, when they use rapeseed oil instead of vacuum gasoil in their cracking experiments. Similar results have been obtained by Carlos de Medeiros *et al.* (1985), whose yield to gasoline in OLP is increased by 8.6 points when they crack soybean oil instead of the typical vacuum gasoil. This better crackability of triglyceride-based biomass is also clearly confirmed by the research group of Melero *et al.* (2010b) in their gasoline distribution, where the medium (MN; 90–140°C) and heavy (HN; 140–221°C) naphthas yields are gradually reduced with the presence of vegetable oil in the feedstock (see data in Table 15.3).

Several authors have pointed to the reduction of the heavier fractions with the co-processing of renewable raw materials in the FCC unit (Bromann et al., 1993; Couch, 2007; Carlos de Medeiros et al., 1985; Melero et al., 2010b). Carlos de Medeiros et al. (1985) obtained LCO and DO yields ranging from 16.98% to 11.85% and from 9.98% to 3.33%, respectively, when cracking vacuum gasoil and soybean oil in FCC conditions. Similar results have been described by Holmgren et al. (2007), and LCO and DO yields changed from 9.5% to 5.0% and from 5% to 3%, respectively, if they crack a triglyceride-based feedstock instead of vacuum gasoil in the FCC unit. LCO is obtained either by means of the heavier fractions cracking or polymerization reactions. In case of the renewable raw materials based on triglycerides, most of the fatty acids of the initial molecules have a length similar to the hydrocarbons in the LCO range as well as an easier trend to be cracked. Something similar takes place with the DO fraction, whereas in the case of petrol feedstocks, it is mainly referred to the percentage of unconverted feed, and in the case of renewable raw materials, DO is always produced via polymerization reactions of olefins and aromatic rings. Triglycerides will be decomposed in reaction conditions, leading to free fatty acids that are never longer than a  $C_{22}$  (DO fraction is in a range of  $C_{18}$ - $C_{30}$  approximately). Since DO is heavier than LCO, its formation by means of polymerization reactions will be more hindered, and hence this fraction being dramatically reduced with the presence of renewable feedstocks in the feed. Thus, DO yield can be remarkably reduced (even more than a 75%) by the presence of a renewable raw material in comparison with the petrol feedstocks (Fig. 15.6).

Considering that polymerization reactions play a significant role when renewable raw materials are processed in FCC conditions, it is interesting the study of the aromaticity of the final liquid product. The aromaticity of the FCC liquid product is enhanced by the presence of vegetable oils and animal fats in the initial feedstock (Bormann *et al.*, 1993; Carlos de Medeiros *et al.*, 1985; Melero *et al.*, 2010b). Data in Table 15.3 also evidence that the presence of renewable raw materials in the feedstock induces changes in the distribution of aromatic rings. The presence of polyaromatic species in the untreated petrol feedstocks leads to higher yields of these refractory compounds since they remain in the final products. Vegetable oils do not have these heavy compounds in their initial composition. Therefore, the cracking product from a triglyceride-based biomass always has lower polyaromatic content than the cracking product of vacuum gasoil. A different trend is observed for the case of monoaromatic (in the range of gasoline) and diaromatic (in the range of diesel) compounds because, although they are absent in the initial vegetable oils, they are easier to form than polyaromatic compounds, especially in the presence of renewable raw materials in the feedstock (Melero *et al.*, 2010b).

Obviously, in the same way that excessive hydrogen elimination from hydrocarbons would produce a higher yield of aromatic compounds, if the removal of hydrogen continues, an increase in the coke production will be observed (highly favoured in case of the renewable raw materials because of the water formation) (Dupain *et al.*, 2007; Melero *et al.*, 2010b). Therefore, coke production is enhanced with the increase of triglyceride-based biomass in the feedstock (Buchsbaum *et al.*, 2004; Carlos de Medeiros *et al.*, 1985; Melero *et al.*, 2010b; Ramakrishan, 2004), as clearly stated in Fig. 15.6.

Finally, some studies of the co-processing of triglyceride-based feedstocks with different features have been performed under FCC conditions. These preliminary studies indicate that the most saturated vegetable oils and animal fats lead to higher LPG yields and lower yields to liquid products as compared with more unsaturated feedstocks (Melero *et al.*, 2010b). On the other hand, the co-processing of crude and refined vegetable oils might induce some deactivation of the FCC catalyst. Wlaschitz *et al.* (2004) have reported that the conversion can be reduced to 5.4% when crude feedstock is processed. These data are in agreement with the trend depicted by Chew and Bhatia (2009), who observed a slight decrease in the final conversion from 72.9% to 70.9% when they cracked unblended crude PO and used PO, respectively, under FCC conditions.

### 15.5 Future trends

The use of cellulosic biomass in a petroleum refinery needs to overcome the recalcitrant nature of this material and convert it into a liquid product, which is done by fast pyrolysis or liquefaction to produce bio-oils or by hydrolysis routes to produce aqueous sugars and solid lignin. Catalytic cracking of bio-oils, sugars and lignin produces olefins and aromatics from biomass-derived feedstocks. Unfortunately, large amounts of coke are obtained under cracking of these compounds over acid solid catalysts, and hence, the improvement of reaction conditions must be addressed in the future. Likewise, the obtained hydrocarbon mixture usually contains a relevant presence of oxygenated compounds that limit its use as a transport fuel.

Triglyceride-based biomass has more appealing properties for its processing in FCC units (lower oxygen content, higher effective hydrogen index, close physical properties to conventional FCC streams . . .). Although the results described in literature are very promising, most of them are in laboratory scale and little work
has been addressed in pilot plant under realistic FCC conditions, and hence, we are still far from a commercial stage. Likewise, another issue in mind is the compatibility of these biomass-based streams in the refinery framework upstream FCC unit (storage, transfer lines, heat exchangers . . .). This topic has been poorly addressed in the literature, but it is a crucial key for the utilization of biomass-derived feedstocks in a petroleum refinery.

We honestly think that the co-processing of biomass feedstocks in petrol refineries is an interesting approach to reach the integrated biomass conversion process in bio-refineries. Furthermore, FCC unit and using oleaginous raw material as feedstocks are shown as the most appealing alternatives.

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**Abstract:** Gasification is becoming a most attractive conversion technology for energy production from fossil fuels, as well as an alternative source of biomass. This chapter gives an insight into gasification, beginning with a general introduction. It discusses different types of gasifier, as well as some of the innovative approaches. The last section of this chapter reviews design methods for different types of gasifier.

**Key words:** gasification, gasifier types, gasifier design methods, gasifier modeling.

# 16.1 Introduction

Gasification, once extensively used for transportation and lighting during the Second World War, lost its merits because cheap and easy fuels were commercialized for power production. At present oil reserves are diminishing and coal combustion is creating the problem of environmental contamination with greenhouse gases. Gasification technology is again getting new life. Its growth in the past has been slow but future predictions show a sharp rise. It has become more modern and sophisticated, such that technically it can easily compete with the existing power generation technologies. Rises in fossil fuel prices, their scarcity and penalties for environmental contamination could be other forces driving the economics of gasification and making the technology more attractive, technically, as well as economically.

Gasification is a thermo-chemical process that converts solid carbonaceous feed into a gaseous fuel product in the presence of steam and/or sub-stoichiometric oxygen. The result of gasification is the producer gas, containing carbon monoxide, hydrogen, methane, and some other inert gases. When it is mixed with air, the producer gas can be used in gasoline or diesel engines with little modification. The gaseous product is applied mainly as fuel gas for electricity generation and direct heating. It can also be used as a synthetic gas in the process industry to produce methanol or ammonia. The idea of gasification power generation fits well with the decentralized energy generation concept. A small-scale gasifier system (10–30 KW) would be appropriate for many applications in villages in developing countries.

Theoretically, almost all kinds of biomass can be gasified but, practically, various properties of the materials impose limitations on the quality of gases that can be

produced. Higher volatile matter results in higher tar content, an undesirable product of gasification. Similarly, large particle size, higher moisture content, and ash content pose a lot of technical challenges. The key to successful design of a gasifier is to understand the properties and thermal behavior of the fuel fed to the gasifier.

## 16.1.1 Advantages of gasification technology

Advantages of gasification over combustion are as follows.

- 1. Gasification is a thermo-chemical conversion process, where the feed is converted into more valuable, environmentally friendly gaseous products that can be used for chemical, fuel, and energy production. The gaseous product can be converted to hydrogen or liquid fuels by reforming or by Fischer–Tropsch synthesis, respectively. The objective of combustion, on the other hand, is to thermally destruct the feed material and produce heat.
- 2. There is higher potential for overall energy efficiencies and conversion of difficult-to-handle feed materials into a gaseous fuel that can be handled with greater ease in conventional equipment designed for natural gas. For example, a producer gas flame can easily be burned with low NO<sub>x</sub> emissions, a gas flame can be easily directed to a certain heating zone, and each burner can be controlled easily.
- 3. The volume of gas produced is much lower in gasification than in combustion, thus a relatively smaller unit is required for the gas cleaning process.
- 4. The solid by-products of gasification are char (low-temperature gasification) and slag (high-temperature gasification). Char is used for various applications in the form of activated carbon, while slag, considered as non-hazardous, can be used as admix for road construction material. The by-product from combustion is mainly bottom ash, consisting of the mineral matters and unreacted carbon. The bottom ash is found to have a leaching property, thus it is considered to be hazardous. So, the solid by-products from gasification are useful and also environmentally friendly, while combustion produces a hazardous by-product.

## 16.1.2 Barriers to gasification technology

The gasification system in its commercial development may face the following technical and non-technical challenges (Basu, Acharya, and Dutta, 2009).

#### Technical barriers

 Availability is the most important factor that prevents the wide scale use of gasifiers in the mainstream energy industries. Present day gasifiers have not reached the standard (>90%) expected in utility industries. The 140 MW high-temperature Winkler gasifier of Rheinbrau started with an availability of 45%, which rose to 89% in 1997 (Renzenbrink *et al.*, 1997). This forced EPC to specify a stand-by gasifier in order to meet the overall unit availability matching the industry standard.

- 2. Complex operation due to a large amount of ancillary equipment, such as oxygen separation units (OSU), gas sweeteners, etc.
- 3. Gasification of high alkali biomass (agglomeration problems), RDF, and waste (mercury removal problem).
- 4. Tar control in order to avoid the problems in gas cooling and filtration, as well as its removal without producing toxic waste water.
- 5. Poor carbon conversion is a major problem. It has been less than 90.5%. High carbon levels in ash reduces the ash quality, and deprives the plant owners from the revenue expected from the sale of gasifier ash for their end-use. High carbon in ash imposes an additional burden of disposal cost.

#### Non-technical barriers

Beside the above technical challenges, several other challenges retarded the market penetration of gasification.

- 1. higher investment;
- 2. fuel availability and price level for non-conventional fuels, such as biomass;
- 3. subsidies available for biomass-only plants but not for co-firing;
- 4. economic competitiveness with steam cycles, co-firing, etc.;
- 5. complicated and costly means of power production;
- 6. small difference in efficiency compared with steam cycles.

The economics of gasification are heavily dependent, however, on the nature of the feedstock and on the location of the gasifier relative to both the source of the feedstock and to the ultimate user of the product (see Table 16.1).

# 16.1.3 Status of gasification

Gasifiers have been employed worldwide for a wide range of feedstocks, such as coal, biomass, and various waste materials. Figure 16.1 shows the status of gasification, showing its present and planned capacities. At present the energy production from gasification is around 60 GW<sub>th</sub>. In coming years, the energy production from gasification is set to grow rapidly reaching around 150 GW<sub>th</sub> by 2014, which is 1.5 times more than what is used at present.

Figure 16.2 shows the application of gasification. Presently, the product gas from the gasification process is used for chemical production and makes little contribution to power generation. However, growth of gasification in the future is predicted to be towards power generation.

Gasification will be a 'breakthrough' technology, as it combines the economic advantages of coal with the environmental benefits of natural gas. Because of its

Country	Projects	Туре	Output (MWth)
Austria	Zeltweg BioCoComb project Güssing Pöls bark gasification project	CFB Dual CFB CFB	10 8 35
Brazil	Brazilian BIG-GT demonstration project	CFB	32 (MW <sub>e</sub> )
Denmark	Harboøre project Høgild project Blære project	Updraft Co-current downdraft Two-stage gasification	4 0.5 0.25 (MW <sub>th</sub> ) + 0.1 (MW <sub>e</sub> )
Finland	Lahti Kymijärvi project ECOGAS energy plant, Varkaus	CFB BFB	60 50
Italy	Thermie energy farm project SAFI SpA RDF gasification project	Lurgi CFB CFB	14 (MW <sub>e</sub> ) 6.7 (MW <sub>e</sub> )
The Netherlands	KARA/BTG Amergas BV project	Co-current downdraft Lurgi CFB	0.15 (MW <sub>e</sub> ) 350 (MW <sub>th</sub> ) + 600 (MW <sub>e</sub> )
Sweden	Gotaverken project (Varo) Värnamo project	CFB IGCC	2 18
Switzerland	Pyroforce gasification plant	KHD pyroforce gasifier	0.2 (MW <sub>e</sub> )
United Kinadom	ARBRE project	Low pressure TPS gasifier	8 (MW <sub>e</sub> )
0	Boughton pumping station CHP project Blackwater Valley museum project	Downdraft Downdraft	$\begin{array}{l} \text{0.18} \ (\text{MW}_{\text{th}}) \\ + \ 0.1 \ (\text{MW}_{\text{e}}) \\ \text{0.4} \ (\text{MW}_{\text{th}}) \\ + \ 0.2 \ (\text{MW}_{\text{e}}) \end{array}$
USA	Vermont Battelle/FERCO project	Low pressure Battelle gasifier	15 (MW <sub>e</sub> )

Table 16.1 Gasification projects

Source: Basu et al., 2009.

huge resources, coal will remain a primary energy for power generation. However, environmental concerns will restrict its use. A safe route for the power company will then be to gasify the coal and use the syngas for power generation. Development of IGCC will be seen to increase in the near future as it is proved to be commercially and technically more attractive than convectional power generation. In the coming decades, a first and second generation IGCC plant is projected to be in the market. Gasification also offers an opportunity to capture carbon dioxide at a significantly lower cost as compared with other fossil-fuelbased technologies.

Natural gas has been used for power generation but in greater part for chemical production. In the US more than 70% of chemicals are derived from natural gas



*16.2* Worldwide gasification capacity for different applications (Higman and Burgt, 2008).

and every \$1.00 increase in the cost of natural gas adds \$3.7 billion in costs to the industry (*http://www.clean-energy.us/facts/gasification.htm*). At present, the demand in the US for natural gas has already exceeded the supply, which predicts there will be a rise in price and the chemical industry will look for an alternative option. The only way to replace natural gas is to produce syngas through gasification and then use it for chemical production instead of natural gas. Another major area of gasification will be production of hydrogen, which will eventually reduce the use of petroleum in vehicles.

Waste is considered no longer as a waste; rather it is looked at as an alternative energy source. A commonly used methods for disposing of municipal solid waste is incineration, which is facing huge criticism for not being environmentally friendly, as it emits high amounts of harmful dioxins, as well as  $NO_x$  and  $SO_x$ . Gasification, on the other hand, for being more efficient in breaking down hazardous dioxins and furans into simple gases, has already been seen as an alternative to incineration. Indirect co-firing using a biomass gasifier and then combusting the product gas in a boiler has given new direction to the co-firing system.

Gasification has the advantage of being fuel flexible, as it can take different types of fuel. That is important when fuel prices are volatile and its availability is not reliable.

A technical challenge to gasification could be tar formation. But with the use of a catalyst and some modification in design, the tar can be effectively controlled. With stringent environmental regulations, its cost advantages will be better.

## 16.2 Mechanism of gasification

Solid fuel in the presence of a gasifying agent (air, oxygen, steam) under thermal action undergoes chemical decomposition to produce the useful gas. According to the type of gasifying agent used, the heating value of the product gas obtained will also be different.

The conversion of gasification feedstocks can be divided into several gross stages: (1) decomposition of the original feedstock into volatile matter and char, (2) conversion of the volatile matter by secondary reactions (combustion and reforming), and (3) conversion of the char by 'char gasification' reactions with H<sub>2</sub>O and  $CO_2$  to produce fuel gases (CO, H<sub>2</sub>, CH<sub>4</sub>), in addition to char combustion when oxygen is present. Devolatilization produces a broad spectrum of products, ranging from light gases to tars. The products are strongly dependent on the identity of the feedstock and process conditions, such as heating rate. These products may contain valuable species. Partial reforming of these products by contact with components of the char bed may result in improved gas quality. For example, if fuel gas is the desired product, such conversion could preserve methane while reforming undesirable tars. The progress of such reforming reactions is dependent on the nature of the char, including the inorganic (ash) components, and the type of reactor. The conversion of the entire feedstock to fuel gases by gasification reactions is generally endothermic, and air or oxygen is typically added to heat balance the process. In general, the solid fuel, during gasification, undergoes the following four processes that are more distinct in the case of the moving bed gasifier (such as an up and down draft gasifier) than in the case of fluidized bed gasification. The mechanism of gasification is shown in Fig. 16.3 and explained in detail below.

1 Drying: In this pricess, the moisture in the feedstock is vaporized. The feedstock does is not decompose because the temperature is not high enough to cause any chemical reaction.



16.3 Different steps in gasification.

2 Pyrolysis: During pyrolysis or devolatization, the volatile content of the matter is released from the feedstock and char is left. This reaction occurs in the absence of oxygen and at a temperature around 300–500°C. The reaction occurring in this process is endothermic in nature, thus the heat required is provided by the combustion of the feedstock during the oxidation process.

$$Feedstock = char + volatiles + energy (kJ/kg).$$
[16.1]

3 Oxidations: In this process, the feedstock is combusted with the air supplied. As gasification is an endothermic process, the overall heat required is produced during this process. To maintain a favorable temperature in the gasifier and also avoid the excess dilution of the product gas, an equivalent ratio (actual air supply/stoichiometric air required for complete combustion) is maintained between 0.2–0.4. The reactions taking place in this process are:

$$C + O_2 \to CO_2, \qquad [16.2]$$

$$2H_2 + O_2 \rightarrow 2H_2O.$$
 [16.3]

4 Reduction: In this process, several reactions take place. The product from this process is mainly the gas, consisting of carbon dioxide, hydrogen, methane and carbon monoxide. The following reactions take place:

Boudouard reaction: 
$$C + CO_2 = 2CO$$
, [16.4]

Water-gas reaction: 
$$C + H_2O = CO + H_2$$
, [16.5]

Methane reaction:  $C + 2H_2 = CH_2$ , [16.6]

Water–gas shift reaction: 
$$CO + H_2O = CO_2 + H_2$$
. [16.7]

The aforementioned reactions are the major gasification reactions. Depending upon the operating conditions, one reaction dominates over another and, thus, the product composition changes accordingly. For example, if steam gasification is used then the reactions [16.5] and [16.7] would be major ones and it can be seen that increasing temperature increases reaction [16.5] while decreasing reaction [16.7]. Similarly, if it is air or oxygen gasification, then reaction [16.4] will be the major one that increases with rise in temperature. Thus, air/oxygen gasification will have a higher concentration of CO.

## 16.3 Factors affecting performance of gasification

Gasification output greatly depends on the properties of the feedstock used, as well as on the operating conditions. Some of the factors are listed below:

1 Ultimate analysis of the feedstock: This determines the chemical composition of the type of fuels. Figure 16.4 shows the C-H-O diagram, which demonstrates that liquid fuel only consists of carbon and hydrogen. In solid fuel, carbon and charcoal have less oxygen and biomass has a higher percentage of oxygen. It



16.4 C-H-O diagram (www.woodgas.com).

also shows the transition from gasification to combustion. The line  $H_2O-CO_2$  is the axis line for combustion; beyond this all fuel gets combusted. The H–CO line is the axis line for gasification.

2 Moisture content, volatile matter, and ash content of the feedstock: Through proximate analysis of the fuel one can identify the moisture content, volatile matter, and ash content of the feedstock. Fuel with low moisture content is desirable because higher moisture content requires more energy to evaporate liquid forms of moisture. In other words, for a given heat input, high moisture fuel will result in a lower temperature, which will effect the composition of gas produced, resulting in a lower heating value gas. Quaak et al. (1998) suggested that, for downdraft gasification, the moisture content of the feedstock should be less than 25%.

During pyrolysis, the volatile matter in a feedstock is released. This volatile matter mainly consists of organic compounds, commonly known as tar. Tar is classified as primary, secondary, and tertiary. The change of tar from one form to another depends on the temperature. Higher temperatures result in tertiary tar. Tar generally condenses in the cooler part of the gasifier and poses many operating problems, like choking of the pipes. If tar cannot be cracked well, it will cause a problem when the producer gas is used in an engine. Thus, a lower volatile feedstock is better suited for engine applications. However, proper design of the gasifier could also help in tar reduction; for example, using a two-stage gasification process could potentially reduce tar because of a higher oxidation temperature (Bhattacharya *et al.*, 2001).

Ash is the mineral content in fuel or feedstock remaining after combustion. In the gasification process, the remaining material is not only ash but also unburned carbon. Ash interferes with the gasification process in two ways:

- (a) It fuses together to form slag and this clinker stops or inhibits the downward flow of the biomass feed in a moving bed gasifier. Even if it does not fuse together, it could offer mass transfer resistance to fuel particles undergoing gasification.
- (b) Some inorganic constituents of the ash have an important catalytic effect on the gasification reaction rate of the char.

High ash content feedstock means the ash must be continuously removed from the gasifier. In addition, it is possible that agglomeration can take place inside the gasifier when using high ash content feedstock. However, the melting point of the ash depends on the mineral compositions in it.

3 Size and size distribution of feedstock: The size and size distribution affects the pressure drop through the bed of the gasifier. Low particle size can increase pressure drop across the gasifier. However, large feedstock particles also need more time for complete gasification. Moreover, obstruction of the feedstock flow can take place in the case of using large feedstock particles in a moving bed gasifier.

- 4 Bulk density of the feedstock: Fuel with higher bulk density is preferable because it has a higher energy content per unit volume, and is easier to transport and handle. Low bulk density fuel may create a problem with improper flow under gravity, mostly in the case of a fixed bed gasifier. This improper flow may result in low calorific value gaseous fuel, difficulty in transporting it from one place to another, and fuel handling that requires a larger space.
- 5 Energy content of feedstock: The energy content refers to the heating value that affects the energy output of the gasifier. Considering the energy balance, if an adiabatic gasification process is assumed, the reaction temperature of the process depends on the heating value of the feedstock used. For charcoal downdraft gasification, the temperature in the combustion zone is higher than 1100°C, compared with 970°C in the case of wood gasification using the same reactor (Bui, 1996).
- 6 Temperature: Temperature governs most of the reactions taking place during gasification and the composition of the output completely depends on it. High temperatures above 800°C favors the water shift reaction, resulting in higher carbon monoxide in product gas, while temperatures around 650–800°C favor water gas shift reactions, resulting in higher hydrogen production for the case of steam gasification.
- 7 Reactor type: The choice of the types of reactor depends on many factors, one of which could be the type of fuel to be handled. If the fuel is low quality coal, then an entrained bed gasifier can be used. For a wide variety of fuel, a fluidized bed gasifier can be used as it can handle different types of fuel in a wide range of particle sizes. However, if the fuel is of low bulk density and high moisture content and the application small scale, then a fixed bed gasifier will be suitable.

# 16.4 Types of gasifier

Various gasifier technologies have been developed over many decades and tailored to suit specific needs. These processes operate at pressures from atmospheric to >20 bars and at temperatures between ~700–1500°C. According to the way the feedstock is brought in contact with the gasifying agent, the gasifier is classified into the following types.

# 16.4.1 Fixed bed gasifier

Fixed bed gasifiers, which consist of a fixed bed of biomass through which the oxidation medium flows in updraft or downdraft configuration, are simple and reliable designs and can be used to gasify wet biomass economically on a small scale for CHP applications (Wang *et al.*, 2008). However, they produce syngas with large quantities of tar or/and char, due to the low and non-uniform heat and mass transfer between the solid biomass and the gasifying agent

(Wang *et al.*, 2008). The product gas must be extensively cleaned before use. Moreover, the throughput for this type of gasifier is relatively low and, therefore, for large-scale applications, as in the case of biomass to liquid (BTL), with very strict requirements concerning the purity of the syngas, fixed bed gasifiers are considered unsuitable.

There are three types of fixed bed gasifiers, as shown in Fig. 16.5: updraft (counter-current), downdraft (co-current), and cross draft gasifier. In case of the updraft gasifier, the fuel is supplied at the top and the air at the bottom so that fuel moves against the air flow, while in the case of the downdraft, air is introduced above the oxidation zone and the product gas is removed from the bottom. In the case of the cross draft, feedstock moves downward while the product gas leaves in a sideways direction. Figure 16.6 shows temperature distribution along the height of the gasifier (see Table 16.2).

In the case of the updraft gasifier, the tar content of the product gas is high, thus it cannot be used directly for the engine applications. As in an updraft gasifier, the pyrolysis zone lies above the combustion zone; the tar formed does not pass through the combustion zone, thus resulting in higher tar content in the product



16.5 Different types of fixed bed gasifier.



*16.6* Temperature distribution along the height of the gasifier (Higman and Burgt, 2003).

gas. This is the opposite of the downdraft gasifiers, where all the pyrolyzed product passes through the oxidation zone, thus product gas has lower tar content. As in the case of the updraft gasifier, the hot gases pass upward so their energy is available to vaporize the moisture. Due to this property, updraft gasifiers can gasify relatively higher moisture content fuel than downdraft gasifiers. Constriction in the oxidation zone of the downdraft gasifier, however, makes its design more complicated and difficult to scale up. Cross draft gasifiers are used mainly for charcoal gasification. However, during the process, the temperature could reach 1500°C, which could lead to material problems (Stassen and Knoef, 2001).

Figure 16.7 shows different designs of downdraft gasifiers. The Imbert type has a narrow constriction near the oxidization zone for efficient combustion of the fuel. Conversely, the stratified type does not have any narrow constriction, making it easier to design and scale up. Another design is the multi-stage downdraft gasifier, which was developed and tested at the Asian Institute of Technology biomass research laboratory. In this type, air is supplied at two stages. Similarly, in the case of the two-stage gasifier, the biomass is first pyrolyzed in a separate zone and then the tar formed is combusted in another gasification zone to supply the heat required for gasification. This type of gasifier can produce product gas with a tar content well below 50 mg/Nm<sup>3</sup>. In the case of the vortex gasifier, the air is supplied so as to create a vortex that causes the volatile pyrolysis product to move up and in the presence of air become combusted. Although gasification and pyrolysis in the vortex gasifier take place in a single reactor, the tar content in a product gas is similar to that of the multi-stage gasifier (Fock and Thompson, 2001). The multi-fuel downdraft gasifier commercialized in China can be operated with wood, corncobs, hard nut shells, sawdust, and hard coal (see Table 16.3).

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Country	Types	Fuel	Size	Organization/ Project
USA	Downdraft	Hogged wood, stumps	1 MW	CLEW
	Downdraft	Wood chips, corn cobs	40 kW	Stwalley Engg.
Denmark	Updraft	Hazardous, leather waste	2–15 MW	DTI
	Updraft	Straw, wood chips, barks	1–15 MW	VOLUND R&D Center
	Downdraft	Wood residues	0.5 MW	Hollesen Engg.
New Zealand	Downdraft	Wood blocks, chips, coppice willow chips	30 kW	Fluidyne
France	Downdraft	Wood, agricultural residues	100–600 kW	Martezo
UK	Downdraft	Wood chips, hazel nuts, shells, MSW	30 kW	Newcastle University of Technology
	Downdraft	Industrial agricultural wastes	300 kW	Shawton Engineering
Switzerland	Stratified	Woody and agricultural biomass	50–2500 kW	DASAG
	Downdraft	Wood, wood waste	0.25–4 MW	HTV energy
India	Downdraft	Wood chips, rice hulls	100 kg/h	Associated Engineering Works
	Downdraft	Wood stalks, cobs, shells, rice husk	NA	Ankur Scientific Energy Technologies
Belgium	Small scale	Wood chips	160 kW	SRC Gazel
South Africa	Downdraft	Wood blocks, chips, briquettes	30–500 kW	SystBM Johansson gas producers
Finland	BIONEER	Wood chips, straw, RDF	4–5 MW	Ahlstrom Corporation
	Updraft	Pellets, peat	6.4 MW	VTT
The Netherlands	Downdraft	Rice husk	150 kW	KARA Energy Systems
China	Downdraft	Sawdust	200 kW	Huairou wood equipment
	Downdraft	Crop residues	300 kW	Huantai integrate gas-supply system

Table 16	6.2 Data	base of	fixed	bed	gasifier
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Source: Chopra and Jain, 2007.





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	Diameter (m)	Superficial velocity (m/s)	Hearth load (m <sup>3</sup> /cm <sup>2</sup> h)
Imbert gasifier	0.15	2.5	0.9
Ū.	0.3	0.63	0.23
Biomass Corporation	0.3	0.95	0.34
	0.61	0.24	0.09
SERI air/oxygen	0.15	0.28	0.1
	0.15	0.24	0.09
Buck Rogers	0.61	0.13	0.05
U U	0.61	0.23	0.08
Syn-Gas Inc.	0.76	1.71	0.62
	0.76	1.07	0.39

	Table 16.3 Diameter	, superficial	velocity and	hearth loa	ad of different	t gasifier types
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Source: Reed and Das, 1998.

## 16.4.2 Fluidized bed gasifier

The first fluidized bed gasifier was developed by Fritz Winkler of Germany in 1921. It was later used for powering gas engines. From 1921, several companies were involved in making fluidized bed gasifiers which proved to be more efficient and competitive with other technology.

These types of gasifiers provide excellent gas–solid mixing. Fluidized bed gasifiers can be operated at lower temperatures – around 800–900°C – than fixed bed gasifiers. This directly affects  $NO_x$  emission reduction. Also better fuel flexibility and efficiency in process carbon dioxide capture are some of the advantages of this type of gasifier.

A fluidized bed gasifier mainly consists of a bed of hot solid that is fluidized by the gasifying agent (air, oxygen, or steam). When the feedstock is fed into the hot bed, it undergoes gasification in the presence of a gasifying agent and the product gas leaves from the top of the gasifier. If the bed solid leaving the furnace is captured and again re-circulated into the gasifier, it is called a circulating fluidized bed (CFB) and if not then it is a bubbling fluidized bed (BFB). The bubbling bed gasifier is generally operated at a lower velocity (2-2.5 m/s) to ensure particles do not leave the reactor. The circulating fluidized bed is operated at higher velocity (3–5 m/s) and particles leaving the reactor are separated in a cyclone and fed back into reactor. CFB gasifiers are very suitable for large-scale syngas production (Tijmensen et al., 2002; Hamelinck et al., 2004; Wang et al., 2008; Zhang, 2009). CFB gasifiers are also considered to be rather fuel flexible and are most suitable for feedstocks with high volatile matter content and high char reactivity, such as biomass. Moreover, they offer short residence time, high productivity, low char/ tar contents, high cold gas energy efficiency and reduced ash-related problems (Wang et al., 2008). The gas produced by CFB gasifiers, operated at ~900°C contains, however, beside H<sub>2</sub> and CO, considerable amounts of CO<sub>2</sub>, H<sub>2</sub>O, and



*16.8* Temperature distribution along the height of the fluidized bed gasifier (Higman and Burgt, 2003).

hydrocarbons like  $CH_4$ ,  $C_2H_4$ , benzene, and tars. Thus, the product needs further treatment in a catalytic reformer to convert the hydrocarbons to H<sub>2</sub> and CO.

Temperature distribution along the height of the fluidized bed gasifier is shown in Fig. 16.8. In the case of fluidized bed gasifiers, the temperature is more uniformly distributed.

Figure 16.9 shows different types of fluidized bed gasifiers that have been commercially developed. The Winkler gasifier, invented in 1920, was probably the first type of gasifier to use fluidization on an industrial scale to gasify pulverized coal and started with a capacity of 2000 m<sup>3</sup>/h of product gas. Foster Wheeler CFB is an air blown gasifier operating at atmospheric pressure. Depending on the fuel and the application needs, it operates at a temperature within the range of 800– 1000°C. The hot gas from the gasifier passes through a cyclone, which separates most of the solid particles associated with the gas and returns them to the bottom of the gasifier. In the twin reactor gasifier, the pyrolysis, gasification, and combustion take place in different reactors. In the combustion zone, the tar and gas produced during pyrolysis are combusted and heat the inert bed material. The bed material is then circulated into the gasifier and the pyrolysis reactor to supply heat. The char and heat carrier from the pyrolyser are taken into the gasifier. The gasification of char in the presence of steam produces the product gas. The residual char and the heat carriers from the gasifier are taken back into the combustor. This system was developed to overcome the problem of tar. The KBR transport gasifier is a hybrid gasifier having characteristics of both entrained bed gasifier and fluidized bed reactor. The KBR gasifier operates at considerably higher circulation rates, velocities (11-18 m/s), and densities than a conventional circulating fluidized bed. This results in higher throughput, better mixing, and higher mass and heat transfer rates. The solids that are transported are separated from the product gas in two stages and returned to the base of the riser. The gasifier operates at 900–1000°C and 11–18 MPa (Higman and Burgt, 2008). EBARA's TwinRec



*16.9* Different types of fluidized bed gasifier (a): Basu, Acharya, and Kausal (2009); (b): Basu (2006); (d): Steiner *et al.* (2002); (c), (e), and (f): Higman and Burgt (2008)).

Process gasifier is used primarily to recover recyclable materials by removing their organic components through gasification and combustion (Steiner *et al.*, 2002). Bharat Heavy Electrical Limited (BHEL) developed a pressurized fluid bed gasifier to take into account the higher ash conent of coal. Raw product gas from the cyclone is cycled and mixed with the feedstock in the drier zone. Again the feedstock is separated and cooled gas is taken for cleaning while the feedstock is supplied to the gasifier. BHEL is developing a 125 MW<sub>e</sub> IGCC demonstration plant at Auraiya in Uttar Pradesh, India (Higman and Burgt, 2008).

### 16.4.3 Entrained bed gasifier

Most of the gasifiers developed since 1950 are of the entrained flow type. The advantages of using entrained flow gasifiers lie in their flexibility in handling any type of coal as feedstock to produce clean, tar-free product gas. With the development of the Integrated Gasification Combined Cycle (IGCC) as a prospect technology for overcoming greenhouse gas emission issues and being more efficient, use of entrained bed gasifiers will further increase in the future for power generation. Entrained bed gasifiers operating at high pressure can supply the product gas at high pressure to the IGCC system without additional compression.

In the entrained flow gasifier, a dry pulverized solid is gasified with oxygen (much less frequently, air) in co-current flow. The gasification reactions take place in a dense cloud of very fine particles (typically <100  $\mu$ m). The much smaller biomass particles mean that the fuel must be pulverized, which requires somewhat more energy than for the other types of gasifiers. Entrained flow gasifiers operate at high temperature (1300–1500°C) and high pressure (20–50 bar), and thus high throughputs can be achieved (Drift *et al.*, 2004). The high temperatures also mean that tar and methane are not present in the product gas. Thermal efficiency is, however, somewhat lower, as the gas must be cooled before it can be cleaned with existing technology. By far the greatest energy consumption related to entrained bed gasification is in the production of oxygen used for the gasification.

There are two types of entrained bed gasifiers: slagging and non-slagging. One differs from the other by the way in which the ash is removed from the system. If the ash is removed in molten form, then it is of the slagging type. If the ash is removed in solid form, then it is of the non-slagging type. To ensure the proper operation of the slagging type, the flow of molten ash should be 6% of the fuel flow. The non-slagging type is mostly favored if the ash content of the fuel is below 1% (Drift *et al.*, 2004).

To feed the fuel at higher pressure, the size of particles needs to be very small. This limits the use of biomass as fuel, as it is fibrous in nature and very difficult to cut into smaller sizes. Also lower bulk density and low heating value reduces its suitability as fuel for entrained bed gasification. To use biomass as fuel, a larger amount of carrier gas is required. This means higher energy for compression of the gas and also a product gas with a poor heating value due to dilution with the carrier gas. In the case of pneumatic feeding, the power penalty is high. For instance, pressurizing biomass up to 40 bars using pneumatic feeding consumes  $0.025 \text{ kW}_{e}/\text{kW}_{th wood}$  reducing efficiency by  $0.04 \text{ kW}_{syngas}/\text{kW}_{th wood}$  (Drift *et al.*, 2004).

Figure 16.10 shows different types of the entrained bed gasifier. The Siemens EGB gasifier consists of a top fired reactor. The reactants are introduced into the reactor through the single centrally mounted burner. This process has some special advantages: it provides axis symmetrical construction, reducing equipment costs, flow of the reactant is from a single burner, thus reducing the number of points to be controlled, and, lastly, the product gas and slag flow in the same direction, reducing any potential blockage in a slag trap (Higman and Burgt, 2008).

Koppers-Totzek atmospheric process is the first entrained flow slagging gasifier operated in atmospheric pressure. This process has been commercially built mainly for the ammonia manufacturing process. It consists of two-side mounted burners, where a mixture of coal and oxygen are injected. The gas leaving at the top at a temperature around 1500°C is quenched with water first. The reactor has a steam jacket to protect the reactor shell from the high temperature (Higman and Burgt, 2008).

The E-Gas gasifier is a two-stage coal/water slurry feed entrained flow slagging gasifier. It is designed to use sub-bituminous coal. The coal slurry is fed in at the non-slagging stage, where the upward flowing gas gives heat to it, thus the gas exits at a lower temperature. The gas is then passed through a fired tube boiler and is filtered in a hot candle filter. The char is separated out at the hot candle filter and is again taken back to the slagging zone of the gasifier. The slag is quenched in a water bath at the bottom of the slagging reactor (Higman and Burgt, 2003).

The British Gas/Lurgi proposes a novel coal gasifier. It is a dry fed, pressurized, fixed bed slagging gasifier. Oxygen and steam are introduced into the gasifier vessel through sidewall-mounted tuyeres (lances) at the elevation, where combustion and slag formation occur. The coal mixture (coarse coal, fines, briquettes, and flux), which is introduced at the top of the gasifier via a lock hopper system, gradually descends through several process zones. Coal at the top of the bed is dried and devolatilized. The descending coal is transformed into char and then passes into the gasification (reaction) zone. Below this zone, any remaining carbon is oxidized, and the ash content of the coal is liquefied, forming slag. Slag is withdrawn from the slag pool by means of an opening in the hearth plate at the bottom of the gasifier vessel (Phillips).

The Hitachi gasifier is an oxygen blown entrained gasifier where the pulverized coal is fed at two stages. At the upper stage, two burners are arranged tangentially to feed the pulverized coal spirally into the gasifier. This gives a swirl motion to the coal, thus increasing the residence time. Oxygen in excess is supplied at the lower zone to melt the slag. In the upper stage, reaction occurs at relatively lower temperatures in the presence of less oxygen. Thus, the coal particles get de-volatized and the char formed moves down to be reacted with high temperature gas.



*16.10* Different types of entrained bed gasifier (a) and (c), Higman and Burgt (2008); (b), Basu (2006); (d), Higman and Burgt (2008); (e), EPRI/ Advanced Coal Generation).

		Entrained flow gasifier				Entrained flow moving bed gasifier	
		Koppers- Totzek Steam/O <sub>2</sub>	Texaco Water/O <sub>2</sub>	Foster Wheeler Steam/air	Combustion engineer Air	Lurgi slagging Steam/O <sub>2</sub>	Lurgi dry ash Steam/O <sub>2</sub>
Pressure Combustion temperature	Mpa °C	0.13 1925	4 1400	2.5 1370–1540	0.1 1750	2.1 2000	2.5 980–1370
Gas exit temperature	°C	1480	230 (after quenching)	925–1150	925	350–450	370–540
Steam (water)/ oxidant	kg/kg	0.4	0.5	0.05	0	1	4
Oxidant	ka/GJ	52	37	111	139	20	17
Coal residence time	s	1	3	N/A	2.5	0.4	1
Cold gas efficiency	%	75	75	90	69	90	80
co	%	53	53	29	23	61	18
CO,	%	10	12	3	5	3	30
H <sub>2</sub> <sup>2</sup> CH4	%	36	35	15	12	28 7	40 9
N <sub>2</sub>	%			4	1	1	1
GĈV	MJ/ m³	11.3	11.1	6.6	4.2	13.8	11.3

Table 16.4 Comparison of different types of entrained bed gasifier (De Souza, 2004)

The Shell Coal Gasification Process can gasify any type of coal that can be pulverized to the right size and pneumatically transported. Buggenum in The Netherlands was the first IGCC plant built using SCGP with a capacity of 2000 tons/day (see Table 16.4).

#### 16.4.4 Novel gasifier

Some of the novel designs of gasifiers are shown in Fig. 16.11.

The chemical looping gasifier is a novel concept to produce a product gas rich in hydrogen and free from nitrogen and at the same time facilitate carbon dioxide capture using sorbent and its regeneration to produce a pure stream of carbon dioxide. It consists of two reactors; one is a bubbling fluidized bed gasifier where the biomass is gasified with steam in the presence of sorbent calcium oxide. The carbon dioxide produced during gasification is captured by calcium oxide. The calcium carbonate thus formed moves into another reactor: a regenerator working as a fast bed. The regenerator is heated to a temperature of 950°C. At this temperature, the calcium carbonate calcines to calcium oxide and carbon dioxide. The solid calcium oxide is separated in a cyclone and sent to the gasifier, while



(a) Chemical looping gasifier



*16.11* Novel designs of gasifiers (a), Acharya *et al.* (2009); (b), Jinhu *et al.* (2004)).

(Continued)



(c) Rotating fluidized bed

16.11 (c), Wilde and Broqueville (2008).

carbon dioxide is separated for sequestration. A laboratory scale 5 kW unit is being investigated by the authors.

A novel approach of integrating a fluidized bed with an entrained bed has been proposed by Wu *et al.* (2004). The lower portion of the reactor is the fluidized bed where, under a moderate temperature of 1000°C, coal with higher reactivity will be converted. The unconverted char in fly ash is trapped in the cyclone separator and is then fed into two chambers of entrained flow gasifiers, further converting it into useful gases. The entrained flow chamber is maintained at 1200–1400°C. The fly ash may contain 30–70% of the char. This system can be flexible in adjusting the composition of CO and H<sub>2</sub> in the product gas by controlling gasification in the fluidized bed and the entrained bed. An experiment done in a bench scale shows an overall carbon conversion of 95% with a CO and H<sub>2</sub> concentration in the product gas within the range of 78–82%. By adjusting the gasification taking place in fluidized bed and the entrained bed, the H<sub>2</sub>/CO ratio can be varied from 0.70 to 1.25.

The rotating fluidized bed process is based on a new concept of injecting fluidization gas tangentially in the fluidization chamber. The basic principal is that the drag force is overcome by the centrifugal force. With this method, a more uniform fluidization is obtained at high centrifugal forces. Finally, inter-particle van derWaals forces can be overcome, allowing fluidization of very fine particles, such as cohesive (Geldart group C) micro- and nano-particles. The fluidization gas enters tangentially and leaves from the central chimney.

# 16.5 Modeling of the gasifier

Biomass properties such as higher volatile content, higher moisture contents, and complex reaction kinetics create challenges in predicting its performance as a fuel for gasification and make it equally difficult to design a gasifier to obtain the desired output. A number of methods have been proposed and used to predict the performance of fluidized bed biomass gasifier. They are zero dimensional, 1D, 2D, and 3D. Very limited work has been done on 2D and 3D modeling. The most frequently used method is equilibrium modeling, as it is easy and gives a quicker prediction of gasifier performance. Equilibrium modeling is the zero dimensional space independent modeling method and is helpful in identifying the maximum possible conversion of biomass and the theoretical efficiency (Huang and Ramaswamy, 2009). Ramayya et al. (2006) have used a stoichiometric equilibrium model to carry out a feasibility study of the coffee husk fluidized bed gasifier. Adhikari et al. (2007) have used a non-stoichiometric equilibrium model for studying the hydrogen production from steam reformation of glycerine and the optimum condition for higher hydrogen yields was at temperatures higher than 900 K, with a water to glycerine ratio of 9 at atmospheric pressure. Nonstoichiometric equilibrium models have been used for modeling steam gasification of coal and pure carbon fuel to predict production of hydrogen from ethanol in the presence of CaO (Florin and Harris, 2008). Jarungthammachote and Dutta (2007 and 2008) used the stoichiometric model to study a downdraft waste gasifier and non-stoichiometric model for both spout bed and spout fluid bed gasifiers. Thus, equilibrium modeling can be very helpful in modeling fluidized bed gasifiers for use with non-convectional biomass like coffee husks, glycerine, ethanol, etc., whose reaction kinetics are not identified correctly. The equilibrium model considers only the mass and energy balance and does not take into account the kinetics of the reaction, so the results obtained may differ a lot from the practical results.

Gasification consists of homogenous and heterogeneous reactions, whose reaction kinetics, as well as mass and energy transfer phenomenon, depends on the operating conditions, and accordingly the product gas composition and yield changes. To overcome this disadvantage and to predict the gasification performance more closely to reality, different simulators were developed. Nikoo and Mahinpey (2008) have used ASPEN PLUS for simulating an atmospheric bubbling fluidized bed biomass gasifier. The ASPEN PLUS simulator uses Gibbs free energy for simulation of product from homogenous reaction and reaction kinetics for char gasification. A shrinking core model has been used for kinetic modeling. Enden and Lora (2004) used a CSFB simulator to predict the performance of fluidized bed biomass gasifiers in terms of maximum char conversion obtained, as well as the amount of tar present in the gas produced, its hot and cold gas efficiency and the heating value of the gas produced, considering point to point mass and energy balance, chemical reactions kinetics and fluidization dynamics. So, once the preliminary sizing is done, one can use this simulator to evaluate whether the designed gasifier will give the desired performance or not.

Guo *et al.* (2001) have used a hybrid neural network model for simulating a steam fluidized bed gasifier to predicting the gas yield and composition of the gas. Because of its complex nature, it is rarely used for modeling the gasification process.

Other mathematical models were also developed to simulate the fluidized bed biomass gasifier. Raman *et al.* (1981) developed a one dimensional model to study the gasification of feedlot manure. Their work does not consider the devolatilization step and considers only the char gasification and water gas shift reaction. Ji *et al.* (2009) have used a 1D non-isothermal model to study steam gasification of biomass in the fluidized bed. Ergüdenler *et al.* (1997) have developed a kinetic-free homogeneous equilibrium model for predicting the steady state performance of a fluidized bed straw gasifier. The Department of Energy has developed a design chart, but this is for the gasification of coal.

The first step in the design of a gasifier is to define the input and expected output. Depending upon the gasification process choice and its configuration, the input and output parameters can also vary, but in general the input and output could be listed as below:

Design input:

- 1 Fuel
  - (a) Proximate and ultimate analysis
  - (b) Feedstock temperature
- 2 Gasifying medium
  - (a) Choice of the medium steam, oxygen, air, or a mixture in suitable proportion.
  - (b) The gasifying medium may be chosen based on the following criteria:
    - (i) The desired heating value of the product gas.
    - (ii) Hydrogen content of the product gas can be maximized with steam, but if it is not a design priority, oxygen, or air could be a better option.
    - (iii) If an nexpensive source of external heat, such as waste recovery is available, steam is a good choice.
    - (iv) If  $N_2$  in product is not acceptable, steam or oxygen are to be chosen.
    - (v) Capital investment is lowest for air as the medium, followed by that for steam. Much larger investment is needed for an oxygen plant, which consumes a large amount of auxiliary power as well.
- 3 Product
  - (a) Desired composition of product gas
  - (b) Desired heating value
  - (c) Desired output of the gasifier ( $Nm^3/s$  or  $MW_{th}$  produced)

#### Design outputs:

- 1 Geometry
  - (a) Reactor configuration, its cross-section area and height
- 2 Operating parameters
  - (a) Reactor temperature

- (b) Input temperature of the gasifying medium
- (c) Amount and relative proportion of the gasifying medium
- 3 Product
  - (a) Yield of product gas
  - (b) Composition of product gas
- 4 Performance parameters
  - (a) Carbon conversion efficiency
  - (b) Cold gas efficiency

# 16.5.1 Design methods

The design methods for each type of gasifier would be different, as they differ in their operation. We know every reaction is governed by three main parameters: time, temperature, and turbulence. So before going into detail in designing we must be clear about which parameters among these three are most important for each type of the gasifier.

- Fixed bed gasifier: residence time
- Fluidized bed gasifier: turbulence (better mixing)
- Entrained bed gasifier: temperature.

Being that fixed bed gasifiers are governed by residence time does not mean that other factors do not play a role. In fixed bed gasifiers, it is very difficult to create turbulence and it is even more difficult to maintain a uniform temperature difference. Thus, by maintaining higher residence time in the reactor one can get higher conversion. Similarly, in the case of the fluidized bed gasifier, better mixing of the fuel with the bed material can result in higher conversion as the residence time is very small. In the case of the entrained bed gasifier, a very high temperature is maintained, as the residence time is low and mixing is poor. Thus, innovation in entrained bed gasifiers is always focused on how to create better mixing/turbulence or increase residence time in the reactor, while in fluidized bed gasifiers it is focused mainly on increasing the residence time and maintaining uniform temperature. However, in the case of fixed bed gasifiers, new ideas are being researched to develop uniform temperature distribution. In the design process, these key points should always be kept in mind.

There are different approaches to design but every design method consists of two major sections:

- 1 Mass balance: This section identifies the amount of mass that is going into and out of the system.
- 2 Energy balance: This section identifies the amount of energy that is going into and out of the system.

The idea is to first define the system and then identify the correct mass and energy balance for that system.

#### 16.5.2 Equilibrium method

The equilibrium approach is further sub-divided into two models:

- 1 Stoichiometric model
- 2 Non-stoichiometric model.

The Stoichiometric model is based on an equilibrium constant. This method requires knowledge of the specific chemical reactions and reaction paths used for the calculation. It means selecting appropriate chemical reactions, and information concerning the value of the equilibrium constant is required. This method, therefore, is not suitable for complex problems where the chemical formulas of the feed or the reaction equations are not well known. This requires the second model, involving minimization of Gibbs free energy (non-stoichiometric model), which is an effective tool to find composition of gases when the reaction paths are unknown (Florin and Harris, 2008). It is a little more complex but advantageous, as a detailed knowledge of the chemical reaction is not needed.

The following section presents a brief discussion on stoichiometric and nonstoichiometric models of computation for the equilibrium concentration of the product gas. It also discusses energy balance, which is essential for an autothermal gasification reaction.

#### Stoichiometric model

This approach will be illustrated using the example of steam gasification of char.

Let A denote the air supply in kg dry air per kg dry fuel, F the amount of dry fuel required to obtain one normal (at 0°C) cubic meter of the gas and  $X_c$  the carbon content of the fuel (kg carbon/kg dry fuel). This carbon is split between CO, CO<sub>2</sub>, and CH<sub>4</sub> in the product gas. We know that 1 kmol gas occupies 22.4 Nm<sup>3</sup>. So, for 1 Nm<sup>3</sup> of gas produced, one can write the carbon (moles) balance between inflow and outflow streams corresponding to:

$$\frac{FX_{\rm C}}{12} = \frac{\left(V_{\rm CO} + V_{\rm CO_2} - V_{\rm CH_4}\right)}{22.4},$$
[16.8]

where V represents the volumetric fraction of a constituent of the gas.

Similarly, one can develop three more equations balancing hydrogen moles, oxygen moles, and nitrogen moles.

$$\frac{FX_{\rm H}}{2} = \frac{\left(2V_{\rm H_2} + 2V_{\rm H_2O} - 4V_{\rm CH_4}\right)}{22.4},$$
[16.9]

$$\frac{FX_{\rm o}}{2} = \frac{\left(2V_{\rm co_2} + V_{\rm co} + V_{\rm H_2o} + 2V_{\rm o_2}\right)}{22.4},$$
[16.10]

$$\frac{FX_{\rm N}}{2} = \frac{\left(2V_{\rm N_2}\right)}{22.4}$$
[16.11]

We assume the product gas to be made of CO,  $CO_2$ ,  $CH_4$ ,  $H_2$ ,  $H_2O$ ,  $O_2$ , and  $N_2$ . The volume fractions of individual gases make up the total product gas, which is 1 Nm<sup>3</sup> for *F* kg feed. So:

$$V_{\rm CO_2} + V_{\rm CO} + V_{\rm H_2} + V_{\rm CH_4} + V_{\rm H_2O} + V_{\rm O_2} + V_{\rm N_2} = 1.$$
 [16.12]

Together one gets five equations. But it is necessary to find eight unknowns:  $V_{CO}$ ,  $V_{CO_2}$ ,  $V_{CH_4}$ ,  $V_{H_2}$ ,  $V_{H_2O}$ ,  $V_{O_2}$ ,  $V_{N_2}$ , and F, the fuel feed for production of 1 Nm<sup>3</sup> of the product gas. To find the eight unknowns it is necessary to obtain three more equations. These are obtained from reaction kinetics. The following three overall gasification equations are relevant for steam gasification:

Water gas reaction:  $C + H_2O \Leftrightarrow CO + H_2 + 131 \text{ kJ/mol}$  [16.13]

Methanation reaction: 
$$C + 2H_2 \Leftrightarrow CH_4 - 75 \text{ kJ/mol}$$
 [16.14]

Shift reaction: 
$$CO + H_2O \Leftrightarrow H_2 + CO_2 - 41 \text{ kJ/mol}$$
 [16.15]

For oxygen or air-gasification, other relevant sets of equations are to be considered. If allowed, these equations could reach equilibrium when forward and backward reaction rates are equal. Let  $P_{\rm CO}$  and  $P_{\rm CO_2}$  be the partial pressure of CO and CO<sub>2</sub>, respectively, under equilibrium.

The partial pressure of CO,  $P_{CO}$  corresponds to the volume fraction of CO. So,  $P_{CO} = V_{CO}$ . *P* when the pressure of the reactor is *P*.

For the water gas reaction,

$$K_{pW} = \frac{P_{\rm H_2} P_{\rm CO}}{2} = V_{\rm H_2} V_{\rm CO} \frac{P}{V_{\rm H_2O}}.$$
[16.16]

For the shift reaction,

$$K_{pWS} = \frac{P_{\rm H_2} P_{\rm CO_2}}{P_{\rm CO} P_{\rm H_2O}} = \frac{V_{\rm H_2} V_{\rm CO_2}}{V_{\rm CO} V_{\rm H_2O}}.$$
[16.17]

For the Methanation reaction the equilibrium equation is:

$$K_{pm} = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} = \frac{V_{\text{CH}_4}}{V_{\text{H}_2}^2 P}.$$
[16.18]

Values of these equilibrium constants at different temperatures may be taken from Basu (2006, p. 68). Equations [16.8] to [16.12] are solved along with Eq. [16.16] to Eq. [16.18] to get eight unknowns. More details of this method are given in Basu (2006).

#### Non-stoichiometric model

This model is based on the premise that at equilibrium stage, the total Gibbs free energy has to be minimized. The procedure mentioned below is developed for spouted bed gasification by Jarungthammachote and Dutta (2008) and for steam gasification with in-process carbon dioxide capture by Acharya and Dutta (2008). The total Gibbs free energy is given by:

$$G' = \sum_{i=1}^{N} n_i \mu_i,$$
[16.19]

where  $n_i$  = number of moles of species *i*,  $\mu_i$  = chemical potential of species *i* given by,

$$\mu_i = G^o_i + RT \ln\left(\frac{f_i}{f^o_i}\right)$$
[16.20]

 $f_i$  = fugacity of species *i* and  $G^o_i$  and  $f^o_i$  = standard Gibbs free energy and standard fugacity of species *i*.

Equation [16.20] can be written in terms of pressure as

$$\mu_i = G^o_i + RT \ln\left(\frac{\phi P_i}{P^o}\right), \qquad [16.21]$$

where  $\phi$  = fugacity coefficient.

For the ideal gas case at atmospheric conditions

$$\mu_{i} = \Delta G^{o}_{f,i} + RT \ln(y_{i}), \qquad [16.22]$$

where  $y_i$  = mole fraction of gas species *i* 

$$y_i = \frac{n_i}{\text{Total moles in the mixture, } n_{iotal}}$$

 $\Delta G^o_{f,i}$  is the standard Gibbs free energy of formation of species *i* and is set equal to zero for all chemical elements.

Now, substituting equation [16.22] in equation [16.19], we get

$$G^{t} = \sum_{i=1}^{N} n_{i} \Delta G^{o}_{f,i} + \sum_{i=1}^{N} n_{i} RT \ln\left(\frac{n_{i}}{n_{Total}}\right)$$
 [16.23]

The value of  $n_i$  should be found such that the  $G^t$  will be minimum. Lagrange multiplier methods can be used for this purpose. To use this method, the constraints need to be defined. Thus, the constraints can be defined in terms of the elemental balance on both the reactant and product side as:

$$\sum_{i=1}^{N} a_{ij} n_i = A_j, J = 1, 2, 3, \dots, K$$
[16.24]

where  $a_{ij}$  = number of atoms of *j*th element in a mole of *i*th species.  $A_j$  = total number of atoms of *j*th element in the reaction mixtures.

Thus, the Lagrange function (L) is defined as:

$$L = G^{t} - \sum_{J=1}^{K} \lambda_{J} \left( \sum_{i=1}^{N} a_{ij} n_{i} - A_{J} \right),$$
 [16.25]

where  $\lambda = lagrangian$  multiplier. So, to find the extreme point,

$$\left(\frac{\partial L}{\partial n_i}\right) = 0$$
[16.26]

Substituting the value of  $G^t$  from equation [16.23] to equation [16.25] and then taking its partial derivative as defined by equation [16.26]; the final equation will be of the form given by equation [16.27]:

$$\left(\frac{\partial L}{\partial n_i}\right) = \frac{\left(\Delta G_{f,i}^o\right)}{RT} + \ln\left(\frac{n_i}{n_{total}}\right) + \frac{1}{RT}\sum_{J=1}^K \lambda_J a_{ij} \cdot$$
[16.27]

## 16.5.3 Kinetic modeling

The kinetic model has two components: hydrodynamics and reaction kinetics. Both affect the overall gasification and are briefly explained below.

#### Hydrodynamics

A typical fluidized bed gasifier is divided into two zones, the dense zone and the freeboard zone. For the dense zone, the designer needs to compute the size of bubbles, bubble velocity, bubble fraction, and gas exchange between the bubble and the emulsion. Empirical relations for these are available in numerous studies, including Kunii and Levenspiel (1991). The solid distribution profile along the height of the freeboard may be determined using decay factors similar to that given by Kunii and Levenspiel (1991). Gas exchange in this zone is based on being a plug flow riser. More details are given in Nemtsov and Zabaniotou (2008).

#### Reaction kinetics

Gasification reactions proceed at a finite speed, which is largely governed by the reaction rate of the char, as it is the slowest of all reactions. Pyrolysis and gasphase reactions are at least an order of magnitude faster than the char conversion. So, the time taken for heating up and devolatilizing of the fuel is much shorter than the time taken for gasification of the char remaining. Thus, the gasification rate of the char is the controlling parameter. The conversion of the porous char particle may be modeled assuming the process to follow either shrinking particle (diminishing size), shrinking core (diminishing size of the unreacted core), or progressive conversion (diminishing density).

# 16.6 Designing of gasifier

## 16.6.1 Designing of fixed bed gasifier

One-dimensional modeling is generally employed to study the fixed bed gasifier. It is not only simple but also provides a better understanding of the engineering design and process optimization for the fixed bed gasifier. The modeling of updraft gasifier explained below is taken from De Souza (2004).

Figure 16.12 shows the model chart for the updraft gasifier. Here the gasifier is divided into two segments: gas and solid, flowing in a counter current direction.



16.12 One-dimensional model chart for updraft gasifier.
There is continuous exchange of mass and heat along the interface of these two phases in the radial direction. The flow of each phase is assumed to be in plug flow mode. Also, there is no momentum transfer between the phases, which means the velocity profile of one phase is not affected by another. Thus, for the model chart developed, the following equation can be written to represent the mass and energy balance.

Mass balance for gas:

$$u_g \frac{d\rho_{g,j}}{dz} = R_{M,G,j} \qquad 1 \le j \le n_G.$$
 [16.28]

Mass balance for solid:

$$u_s \frac{d\rho_{s,j}}{dz} = R_{M,S,j} \qquad 1 + n_G \le j \le n, \tag{16.29}$$

where  $R_{M,G,j}$  and  $R_{M,S,j}$  is the rate of production if positive and the rate of consumption if negative.  $\rho$  represents the density of the respective phase. *u* represents the velocity of the respective phase.

The mass flux of chemical species j in gas in the z or axial direction is given by

$$\frac{dF_{G,j}}{dz} = S_G R_{M,G,j} \qquad 1 \le j \le n_G$$

$$[16.30]$$

And the mass flux of chemical species *j* in the solid is given by

$$\frac{dF_{s,j}}{dz} = S_s R_{M,s,j} \qquad 1 \le j \le n_G,$$

$$[16.31]$$

where  $S_{\rm S}$  and  $S_{\rm G}$  are the fraction of area available for the flow of the solid and the gas phases, respectively, and can be defined in terms of the voidage of the reactor,

$$\varepsilon = \frac{V_G}{V}, \quad \frac{S}{S_G} = \frac{1}{\varepsilon}, \quad \frac{S}{S_S} = \frac{1}{1 - \varepsilon},$$
[16.32]

where  $V_{\rm G}$  is the volume occupied by the gas and V is the total bed volume.

The energy balance equation for the gaseous phase and the solid phase can be written as:

$$F_G c_G \frac{dT_G}{dz} = \varepsilon S \Big( R_{Q,G} + \mathbf{R}_{C,G} + \mathbf{R}_{h,G} + \mathbf{R}_{R,G} \Big),$$
[16.33]

$$F_{s}c_{s}\frac{dT_{s}}{dz} = (1-\varepsilon)S\left(R_{Q,s} + R_{C,s} + R_{h,s} + R_{R,s}\right),$$
[16.34]

where  $R_Q$  is the energy source or sink,  $R_C$  is the convective heat transfer,  $R_h$  is the enthalpy addition (or subtraction) from one phase to another due to mass transfer between the phases,  $R_R$  is the radiation heat transfer between the phases. Thus, solving equations [16.28] to [16.34], one can get the composition of the gas and also the conversion of the solid fuel.

#### 16.6.2 Design of fluidized bed gasifier

The preliminary sizes and operating parameters of a fluidized bed gasifier may be estimated as follows:

#### Main flow rates

Using the desired power output (*Q*), the volumetric lower heating value  $(LHV_v)$  of the producer gas and assumed gasifier efficiency, one can calculate the biomass flow rate (*F*) for production of 1 Nm<sup>3</sup> of gas as:

$$F = \frac{Q}{LHV_{v}\eta_{g}} \quad \text{kg/Nm}^{3} \text{ product gas}$$
[16.35]

One can find the required air flow rate,  $M_{air}$  for an air-gasification unit assuming a value of equivalence ratio, *ER* within the range of (0.2–0.3) (Basu, 2006)

$$M_{air} = m_{th}.ER.F$$
 kg air/Nm<sup>3</sup> product gas, [16.36]

where  $m_{th}$  is the stoichiometric amount of air kg/kg and F is the fuel feed rate.

For steam gasification gasifiers, one can use published data on the steam/ biomass ratio for a similar fuel to find the amount of the gasification medium  $M_{med}$ as the first guess.

As the gasifying agent will also be the fluidizing gas, it is necessary to check that it would be adequate for proper fluidization. The fluidizing velocity is chosen based on the bed particle characteristics taking into consideration the bed hydrodynamics and the process occurring in gasifier.

#### Reactor dimension

The volume flow rate of the gasifying medium (steam/air or oxygen) divided by the chosen fluidizing velocity will give the reactor cross-section area.

$$A_{bed} = \frac{M_{med}}{\rho_{med}U},$$
[16.37]

where  $\rho_{med}$  and U are the density and the fluidization velocity of the medium (air, oxygen, steam, or their mixture) at the operating bed temperature, respectively.

#### Bed height

The bed height should be chosen such that it provides the required residence time for better carbon conversion and would avoid slugging. Also, its selection is governed by operating cost considerations, as higher bed height means a higher pressure drop, taller reactor, and greater auxiliary power consumption.

#### Freeboard height and its diameter

Ideally, the freeboard height should exceed the transport disengaging height (TDH), so that the particle entrainment with upward flowing gases will be low, but in most cases, that is too expensive. A compromise between cost and performance is used.

## 16.6.3 Design of entrained bed gasifier

Figure 16.13 is a schematic diagram of the entrained bed coal gasifier when the solid fuel and gaseous stream are flowing in same direction. Entrained bed gasifiers are generally modeled as plug flow reactors. Now, as the solid fuel flows along with gaseous stream, it undergoes several reaction intensities depending on different operating parameters (like temperature, pressure, concentration, and time). During the whole process, there is continuous exchange of mass and energy between the gaseous and solid fuels.

Development of the model for the entrained bed gasifier is divided into three parts: (a) mass balance, (b) determination of the equation for calculating reaction rates, and (c) heat balance. Thus, the iteration of the equations developed from these three parts will give the desired output.

Figure 16.13 shows the model chart for the entrained flow reactor. Here it is assumed that the solid particles and gas are in one-dimensional plug flow in the axial direction and radially well mixed. For this case, the mass balance equation can be written as:

Mass balance for solid component

$$\frac{dW_s}{dL} = -N_v A \sum_{k=1}^5 r_k(T_s, L),$$
[16.38]



16.13 Schematic diagram of entrained bed gasifier (Vamvuka et al., 1995).

$$W_s = W_{so}(1 - X_s),$$
 [16.39]

where  $W_s$  = flow rate of the solid (g/s),  $W_{so}$  = initial solid (g),  $N_V$  = number of coal particles per unit volume, A = cross sectional area of the gasifier (cm<sup>2</sup>),  $T_s$  = temperature of the solid (K), L = gasifier length (cm), r = rate of solid gas reaction (gs<sup>-1</sup>),  $X_s$  = solid conversion.

Mass balance for the gas component

$$\frac{dF_{gl}}{dL} = \pm N_{\nu}A \sum_{k=1}^{5} V_{lk} r_k(T_s, L), \qquad [16.40]$$

$$F'_{gl} = F_{glo} + \sum_{k=1}^{5} v_{lk} \xi_k, \qquad [16.41]$$

where  $F_{gl}$  = flow rate of gas (mol s<sup>-1</sup>),  $v_{lk}$  = stoichiometric coefficient for the  $l_{th}$  gaseous components in  $k_{th}$  solid gas reaction,  $\xi$  = extent of reaction (mol s<sup>-1</sup>).

Now the diffusion of the gaseous component into the solid component is governed by the reaction rates. Thus, the overall reaction rates can be defined as:

$$r_s(T_s, L) = N \sum_{k=1}^{5} r_k(T_s, L) dt,$$
[16.42]

where,  $r_k(T_s, L) = \chi_{sk}(T_s)(Py_{ls})^n 4\pi r_{ps}^2$ , k = 1, ..., 5, N = number of coal particles per sec (s<sup>-1</sup>),  $\chi =$  surface reaction rate coefficient (gs<sup>-1</sup> cm<sup>-2</sup> atm<sup>-1</sup>), y = mole fraction of the gaseous component.

Using the above equation the coal conversion can be predicted and the size of the particles can be known from the relation:

$$\begin{bmatrix} \sum_{k=1}^{5} a_{lk} r_k(T_s, L) \\ 4\pi r_{ps}^2 \end{bmatrix} = \frac{D_{lm} P}{R' T_g r_{ps}} (y_1),$$
[16.43]

where *a* = amount of gaseous reactant required to react with the unit mass of coal (mol  $g^{-1}$ ), *D* = diffusion coefficient of the gas (cm<sup>2</sup> s<sup>-1</sup>), *R* = universal gas constant (KJ mol<sup>-1</sup> K<sup>-1</sup>).

The expression for the rate of energy transfer (considering conduction and radiation) between the solid and the gas phases is as follows.

For solid phase:

$$\frac{d\left(W_{s}c_{ps}T_{s}\right)}{dL} = -N_{v}A\left[\left(\sum_{k=1}^{5}r_{k}\left(T_{s},L\right)\Delta H_{k}\left(T_{s}\right)\right) + 4\pi r_{ps}^{2}\left(\frac{\lambda_{g}}{r_{ps}}\left(T_{s}-T_{g}\right) + \varepsilon_{p}\sigma\left(T_{s}^{4}-T_{g}^{4}\right)\right)\right]$$
[16.44]

For gas phase:

$$\frac{d\left(\sum_{l}F_{gl}c_{pgl}T_{g}\right)}{dL} = -\left[A\sum_{k=6}^{9}\Delta\xi k\Delta Hk(Tg) + N\nu A\left(\left(\frac{\lambda_{g}}{r_{ps}}\left(T_{s}-T_{g}\right)+\varepsilon_{p}\sigma\left(T_{s}^{4}-T_{g}^{4}\right)\right)4\pi r_{ps}^{2}\right)\right], \qquad [16.45]$$
$$-\varepsilon_{w}\sigma\left(T_{g}^{4}-T_{w}^{4}\right)\pi D_{i} - h_{c}\left(T_{g}-T_{w}\right)\pi D_{i}$$

where  $c_{ps}$  = specific heat capacity of the solid (J g<sup>-1</sup> K<sup>-1</sup>),  $\Delta H$  = heat of the reaction (cal g<sup>-1</sup>),  $\lambda$  = thermal conductivity (cal s<sup>-1</sup> cm<sup>-1</sup> K<sup>-1</sup>),  $\varepsilon$  = emissivity,  $\sigma$  = Stefanboltzman constant (cal s<sup>-1</sup> cm<sup>-2</sup> K<sup>-4</sup>),  $D_i$  = internal diameter of the gasifier (cm).

Thus, the system of non-linear equations is developed by conducting mass and energy balance. By solving this system the composition of different product gases can be obtained.

The relation of the dimension (length, diameter, and thickness of the entrained reactor and the primary and secondary nozzle diameter) with coal capacity has been developed by Kim and Kim (1996). The results are shown in Fig. 16.14.



16.14 Design graphs for entrained bed gasifiers (Kim and Kim, 1996).

#### 16.7 Conclusions

To secure a quality of life for current and future generations, sufficient water, land, and energy must be available. It is generally recognized that human development cannot continue to depend on fossil fuels in the present manner forever. Therefore, the issue is not whether renewable biofuels will play a role in providing energy but to what extent, and what the implications of their use will be for the economy, for the environment, and for the global security. What is seldom mentioned is that even in a 'sustainable world' not only energy but also carbon for organic chemicals, including plastics, is required.

Over the years, we have seen that the principal roles of syngas have shifted from domestic heating fuel, to feedstock for Fischer–Tropsch (F–T), to petrochemical feedstocks, to starting materials for alternative fuels, to IGCC, and to hydrogen sources. The only way to produce these useful resources from waste and biomass is to first gasify them in order to make syngas. In electric power generation, IGCC has contributed tremendously to improvement of power generation efficiency, thus keeping the cost of electric power competitive against all other forms of energy. Interest in methanol and dimethylether is revived due to the ever-rising cost of conventional clean liquid fuel. With the advent of hydrogen economy, there is no doubt that the use of hydrogen in combination with fuel cells as a transport fuel will improve the climate by eliminating  $CO_2$ ,  $NO_x$ , CO, hydrocarbon, and soot emissions – and this is a prospect that could become reality within two decades.

The issue here is how to produce this hydrogen and make it available in a useable form. Gasification, coupled with water-gas shift, is the most widely practiced process route for biomass to hydrogen; however, it needs to be refined further. It is our opinion that gasification can and will have an important role to play in the coming decades. Therefore, more advances are expected in the areas of product gas cleaning, separation and purification, feedstock flexibility and feeding, disposition of ash/slag, plant availability, economics of scale, and integrated or combined process concepts.

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**Abstract:** This chapter discusses developments and possibilities in the field of alcohol production via synthesis gas based on biomass feedstocks. The most promising technologies based on biomass gasification are believed to be the catalytic and the biocatalytic routes. Biobased synthesis gas fermentation processes to methanol, ethanol and even butanol are being developed. The main bottleneck for these fermentation based processes are still the relatively low concentrations of alcohol in water (<5 wt%), which can be reached with bacteria. New alcohol–water separation processes are needed to make these processes become feasible.

Key words: gasification, bioalcohol, biocatalyst, fermentation, synthesis gas.

## 17.1 Introduction

Alcohol production via gasification is already a very well established process for methanol production. In fact most of the methanol produced nowadays is based on the catalytical conversion of synthesis gas (*Ullmann's Encyclopedia of Industrial Chemistry*, 2001). The synthesis gas is being produced from fossil fuels, e.g. natural gas. For the higher alcohols these routes are not so common. Ethanol being the second largest alcohol produced is mainly produced via fermentation of sugars and for a smaller part via direct hydrolysis of ethylene. Research and developments are focused on production of ethanol directly from synthesis gas via a (bio)catalytical route making the synthesis gas route more interesting. Besides methanol and ethanol the most important alcohols are 1-propanol, 1-butanol, 2-methyl-1-propanol (isobutyl alcohol), the plasticiser alcohols ( $C_6 - C_{11}$ ), and the fatty alcohols ( $C_{12} - C_{18}$ ), used for detergents. They are prepared mainly from olefins via the oxo synthesis, or by the Ziegler process (*Ullmann's Encyclopedia of Industrial Chemistry*, 2001).

The aim of this chapter is to enlighten and discuss more the developments and possibilities in the field of alcohol production via synthesis gas based on biomass feedstocks. Environmental effects (greenhouse gas emissions), demand for independencies on fossil fuels and rising costs of fossil fuels have set an urge to diversify feedstocks and use biomass also as a chemical resource.

Since the 1970s the interest for the use of biomass as feedstock for chemicals and fuels has risen and resulted in an increase in the fermentation processes for ethanol especially as a fuel for automotive purposes. Also the increase in the use of biodiesel which contains 10 wt% methanol has increased the demand for biobased methanol. Disadvantage of the fermentation routes of ethanol is that they can only convert sugar into ethanol, limiting the biomass feedstock from an economical and efficiency point of view to high yield sugar containing crops like sugar cane and sugar rich waste streams.

Gasification of biomass and subsequent conversion of the synthesis gas produced to alcohols would overcome these disadvantages. The problem with the present factories for methanol production is that they are based on a very large scale input (mainly natural gas) which means that very large amounts of biomass will have to be transported to one location. This is not economically attractive. Many options have been suggested such as to convert the biomass via digestion into methane which can be transported via pipelines to the factory. This means building up a pipe line infrastructure with subsequent high investment costs. Another route tried at a large methanol plant in Delfzijl in The Netherlands is to convert the glycerol byproduct from biodiesel production facilities into methanol via gasification (BioMCN, 2009). Disadvantage for this route is that there is a hydrogen shortage which has to be added from other sources.

The most promising technologies based on biomass gasification are believed to be the catalytic and the biocatalytic routes. The idea is in both case the same: convert synthesis gas via a (bio)catalyst into alcohols. Methanol is very difficult to achieve with biocatalyst because of its more toxic nature. For ethanol, this seems more promising and making smaller scale plants interesting (more fitting to the decentralised character of the biomass production process). Fermentation of the gasification product gas, however, is a rather new development.

Datar *et al.* (2004) have been working on the fermentation of producer gas, and have successfully produced ethanol. Figure 17.1 shows the schematic of the



17.1 Schematic drawing of biomass to ethanol process.

biomass to ethanol process. The idea is to gasify the biomass to synthesis gas  $(CO + H_2)$  and subsequently ferment this biosynthesis gas to ethanol via a direct fermentation process. The first step is to gasify the biomass input to synthesis gas.

The gasification/fermentation pathway is a very interesting alternative way of producing bioethanol. Via traditional fermentation processes, lignin, an important component of biomass cannot be fermented. Gasification and subsequent fermentation of the produced gas enables fermentation of all carbon and hydrogen containing material and also non biodegradable materials like plastics. The resulting higher feedstock efficiency should make the biobased, smaller scale processes economically feasible (Van Schijndel and Van Kasteren, 2004).

## 17.2 Gasification routes for alcohol production

## 17.2.1 Introduction

As discussed in the introduction alcohols are produced via the synthesis gas route. The crucial step here is not the synthesis gas production via gasification but the conversion of synthesis gas into alcohols. For methanol this is a common practice although this is not straightforward: high pressure (50–100 bars), the right composition and purity of CO and H<sub>2</sub> is necessary. For ethanol a number of synthesis routes have been proposed. Table 17.1 shows possible routes for ethanol production based on synthesis gas routes. Two routes can be distinguished: direct and indirect synthesis via intermediate products. The direct route would be the most interesting route from a molecular efficiency point of view, but the present catalytic systems (Cu-Zn-Co oxides/halides, Rh(CO)<sub>12</sub> on La<sub>2</sub>O<sub>3</sub>) only produce ethanol production is still the most used one. Of this last method there are again different kind of options among which are homologation (= chain extention) and a sequence of carbonylation, esterification and hydrogenation.

## 17.2.2 Hydrocarbonylation van methanol to ethanol

The hydrocarbonylation is a synthesis gas based route via which extention of the alcohol with a  $CH_2$  group is carried out; in this case the extension of methanol to ethanol:

$$CH_3OH + CO + 2H_2 \Leftrightarrow C_2H_5OH + H_2O$$

By carrying out the reaction in tetrahydrofuran as solvent, good yields can be achieved (89%). The catalysts used in this process are based on metals like Cu, Fe and Ni.

#### 17.2.3 Ethanol synthesis via acetate route

In this route methanol is converted into acetic acid, which can be hydrogenated to ethanol. Monsanto (1968) commercialised this process for the production of

	Typica	l conditio	ons	Yields		
Key step	(Mpa)	(°C)	Phase	Catalysts	Ethanol wt%	By-products
Synthesis gas to ethanol	4.1– 10.1	240– 370	Gas	Cu-Zn-Co oxides/halides	28	Methanol, higher alcohols, HCs
Synthesis gas to ethanol	6.1	250	Gas	Cu-Co oxides, alkali metal oxides	35	Methanol, propanol, butanol
Synthesis gas to ethanol	0.1	220	Gas	Rh(CO) <sub>12</sub> on La <sub>2</sub> O <sub>3</sub>	49	Methanol CH <sub>4</sub> , CO <sub>2</sub>
Methanol and CO to ethanol		220	Liquid	Fe(CO) <sub>5</sub> - Mn <sub>2</sub> (CO) <sub>10</sub> .R <sub>3</sub> N	72	$CH_4$
Methanol and CO to ethanol	27.6– 34.5	200	Liquid	Co-Ru halides	60–80	Higher alcohols, acetates, esters
Methanol to acetaldehyde	24.1	180	Liquid	Group VIII halides	80–90	Higher alcohols, acetates, esters
Methanol to ethanol		220	Liquid	Fe(CO) <sub>5</sub> - Co(CO) <sub>8</sub> .R <sub>3</sub> N	High	
Acetic acid and H <sub>2</sub> to ethanol	12.4	250	Liquid	Cu-Co-Mn-Mo oxides	High	

Table 17.1 Production of ethanol via synthesis gas based routes

acetic acid from methanol. The hydrogenation of acetic acid is possible but has to take place at high pressures and the mixture is highly corrosive which does not make it an attractive process.

Alternatively Davy McKee has patented the conversion of acetic acid with ethanol to ethyl acetate (temperature 175°C, pressure 7 MPa), which can be hydrogenated to two ethanol molecules thus rendering a net production of ethanol (Bradley *et al.*, 1983). The last reaction can take place at 200°C with a Cu/ZnO catalyst.

The total reaction scheme is:

$$\begin{split} & \mathrm{CH}_{3}\mathrm{OH} + \mathrm{CO} \rightarrow \mathrm{CH}_{3}\mathrm{COOH} \\ & \mathrm{CH}_{3}\mathrm{COOH} + \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH} \rightarrow \mathrm{CH}_{3}\mathrm{COOC}_{2}\mathrm{H}_{5} + \mathrm{H}_{2}\mathrm{O} \\ & \mathrm{CH}_{3}\mathrm{COOC}_{2}\mathrm{H}_{5} + \mathrm{H}_{2} \rightarrow 2\,\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH} \end{split}$$

The net reaction is:

 $CH_3OH + CO + H_2 \rightarrow C_2H_5OH + H_2O$ 

A variation on this concept has been developed by the Halcon SD group (Porcelli and Juran, 1985). In this process methyl acetate is carbonylated instead of

methanol. The resulting anhydride forms together with ethanol and methanol two different acetates. After separation the ethyl acetate is hydrogenated to ethanol and the methyl acetate is recycled to be carbonylated again.

$$CH_{3}COOCH_{3} + CO \rightarrow (CH_{3}CO)_{2}O$$
$$(CH_{3}CO)_{2}O + CH_{3}OH + C_{2}H_{5}OH \rightarrow CH_{3}COOCH_{3} + CH_{3}COOC_{2}H_{5}OH$$

Alternatively ethanol can be produced via ethylene which can be converted to ethanol via the existing catalytic hydrolysis of ethylene. Overall yields are however not very high and it looks more promising nowadays to produce ethylene from ethanol via sugar fermentation processes making bio-ethylene production possible rather than the other way around.<sup>1</sup>

## 17.2.4 The direct hydrolysis of ethylene to ethanol

Ethylene  $(C_2H_4)$  reacts with water to form ethanol via a catalytic addition reaction. The yield of ethanol production is determined by the equilibrium of the reaction:

$$C_2H_4(g) + H_2O(g) \Leftrightarrow C_2H_5OH(g) \Delta H = -43.4 \text{ kJ/mol}$$

The catalyst used is phosphoric acid (silica gel based), which sets some demanding standards concerning corrosion of the equipment.

The equilibrium reaction is influenced by temperature, pressure and the ratio of water to ethylene. Normal process conditions are equimolar concentrations,  $250-300^{\circ}$ C and 5–8 MPa, resulting in a conversion degree of only 7–22%. A lower temperature favours the ethanol production, but also favours the side reaction to diethyl ether:

$$C_2H_5OH(g) + C_2H_4(g) \Leftrightarrow C_2H_5OC_2H_5(g)$$

Too high pressure is also not favourable because higher alcohols will be formed:

$$C_2H_4(g) \Leftrightarrow C_4H_8(g) + H_2O(g) \Leftrightarrow C_4H_9OH(g)$$

#### 17.2.5 The indirect hydrolysis of ethylene

The indirect hydrolysis of ethylene takes place with the aid of sulphuric acid. Ethylene is dissolved in concentrated sulphuric acid. Addition of water leads to the production of ethanol and some diethyl ether as side product:

$$\begin{split} &C_2H_4 + H_2SO_4 \Leftrightarrow C_2H_5OSO_3H \, \Delta H = -60 \text{ kJ/mol} \\ &C_2H_4 + C_2H_5OSO_3H \Leftrightarrow C_2H_5OSO_2OC_2H_5 \end{split}$$

Hydrolysis after addition of water:

$$\begin{split} & C_2H_5OSO_3H + H_2O \Leftrightarrow C_2H_5OH + H_2SO_4 \\ & C_2H_5OSO_2OC_2H_5 + H_2O \Leftrightarrow C_2H_5OH + C_2H_5OSO_3H \end{split}$$

Side reaction with water to form diethyl ether:

$$C_2H_5OSO_2OC_2H_5 + C_2H_5OH \Leftrightarrow C_2H_5OC_2H_5 + C_2H_5OSO_3H$$

Dependent on reaction conditions 5-10% diethyl ether is formed during reaction. The use of concentrated sulphuric acid sets high standards for the equipment due to the corrosive character.

Conclusion is that for the chemical routes the direct route is not economically attractive and that the indirect routes are the best up to now, although relatively cumbersome. This is the reason that the biological route of sugars to ethanol is economical, interesting and also remains to be a good alternative for ethanol production.

Newest developments focus on a combination of gasification and biological fermentation processes. After gasification, anaerobic bacteria such as *Clostridium ljungdahlii* are used to convert the CO,  $CO_2$  and  $H_2$  into ethanol. Higher rates are obtained because the process is limited by the transfer of gas into the liquid phase instead of the rate of substrate uptake by the bacteria.<sup>2</sup>

Subsequent conversion of the formed synthesis gas to ethanol brings the formation of ethanol from a diversity of biomass sources into reach. Two routes can be followed in this respect: catalytic conversion of the synthesis gas via the routes shown in Table 17.1 or biological route via direct fermentation. For smaller scale installations (<100 Kton) this last route seems to be interesting compared to the catalytic route. The catalytic route needs a catalyst which is always sensitive to deactivation via pollution in the feedstock. Also catalysts are relatively expensive. This leads to high investment cost for cleaning (on ppm level) of synthesis gas and thus economically attractive at large scale processes only. The direct biological route seems more promising for smaller scale systems because they can endure pollution of the synthesis gas and low cost fermenters can be used at ambient process conditions. Fermentation tests for ethanol production from synthesis gas have been done in various reactor types. Phillips and others (1994) used a stirred batch reactor. Klasson and others (1990) used several continuous reactors, namely a stirred-tank reactor, a packed bubble column and a trickle-bed reactor. The processes take place at 37°C, and the pH is controlled. A frequently used bacterium is *Clostridium ljungdahlii*. This bacterium produces acetic acid as a side-product.

$$\begin{split} \text{CO} + 1/2\text{H}_2\text{O} &\rightarrow 1/6\text{C}_2\text{H}_5\text{OH} + 2/3\text{CO}_2 & \Delta\text{G}^\circ = -216 \text{ kJ/mole ethanol} \\ \Delta\text{H}^\circ = -331\text{kJ/mole ethanol} \\ \text{H}_2 + 1/3\text{CO}_2 &\rightarrow 1/6\text{C}_2\text{H}_5\text{OH} + 1/2\text{H}_2\text{O} & \Delta\text{G}^\circ = -97.1 \text{ kJ/mole ethanol} \\ \Delta\text{H}^\circ = -349 \text{ kJ/mole ethanol} \\ \text{CO} + 1/2\text{H}_2\text{O} &\rightarrow 1/4\text{CH}_3\text{COOH} + 1/2\text{CO}_2 & \Delta\text{G}^\circ = -135 \text{ kJ/mol acetic acid} \\ \text{H}_2 + 1/2\text{CO}_2 &\rightarrow 1/4 \text{ CH}_3\text{COOH} + 1/2\text{H}_2\text{O} & \Delta\text{G}^\circ = -54.8 \text{ kJ/mol ethanol} \end{split}$$

In the ideal case (no side-products) this results in the following overall theoretical reaction when starting from pinewood:

CH<sub>1,34</sub>O<sub>0.66</sub> + 0.17O<sub>2</sub> + 0.17H<sub>2</sub>O → 0.28C<sub>2</sub>H<sub>5</sub>OH + 0.44CO<sub>2</sub>  
$$\Delta$$
H° = -59 kJ/mole wood

Overall combustion energy efficiency in the ideal case is  $(LHV_{ethanol}/LHV_{wood}) = 0.28 \times 1233/410 = 84.2\%$ . This means that this route has potential as a possible route for ethanol production from wood.

It has also been shown (Dürre, 2007) that it is possible to produce butanol. Dürre mentions that 'butanol has advantages over ethanol, such as higher energy content, lower water absorption, better blending ability and use in conventional combustion engines without modification. Like ethanol, it can be produced fermentatively or petrochemically. (....) The best-studied bacterium to perform a butanol fermentation is *Clostridium acetobutylicum*. Its genome has been sequenced, and the regulation of solvent formation is under intensive investigation. This opens the possibility to engineer recombinant strains with superior biobutanol-producing ability'. It is also possible to produce butanol from grass and straw via an enzymatic way (www.biobutanol.nl as of January 2010). However, for this route the same disadvantages are valid as for the enzymatic route to ethanol: only the biodegradable fractions can be converted to alcohols.

The question is how far the ideal route can be approached and at what costs. For this reason the next section describes a conceptual design and simulation of a wood to ethanol plant via gasification and direct fermentation. The design is based on literature data and performed with the use of the software package Aspen Plus (Van Kasteren *et al.*, 2005). In the following sections the design assumptions, the input composition, the reactor section and the purification section are described in detail. Other process components are discussed in the general process description.

## 17.3 Conceptual design of a bio waste ethanol plant

#### 17.3.1 Introduction

This section describes the design of a small-scale mixed waste (biomass/plastics) gasifier with a synthesis gas fermentation-unit, which produces ethanol. Part of the synthesis gas will be used for heating up the gasifier and for making electricity (see Fig. 17.2).

Research has been carried out and a design has been made by Van Kasteren *et al.* (2005). This report shows an analysis of the fermentation of synthesis gas to ethanol process with the aid of bacteria. Before fermentation can take place first the biomass has to be gasified and the synthesis gas cleaned. The next section describes the choice of gasifier.

## 17.3.2 Choice of gasifier

A wide range of biomass fuels such as wood, charcoal, wood waste as well as agricultural residues – maize cobs, coconut shells, cereal straws, rice husks can be



17.2 Scheme of a bio waste to ethanol plant.

used as fuel for biomass gasification. Theoretically, almost all kinds of biomass with moisture content of 5-30% can be gasified; however, not every biomass fuel leads to the successful gasification. Most of the development work is carried out with common fuels such as coal, charcoal and wood. Key to a successful design of a gasifier is to understand the properties and the thermal behaviour of fuel as fed to the gasifier. Gasification systems: descriptions are found in Chapter 16 and

elsewhere (Reed and Gaur, 2000). Attention has to be given on tar (also known as creostate, is a sticky, condensable vapour whose main constituents are benzene, toluene, indene, naphthalene and phenol) minimisation during gasification. Its formation is affected by temperature, type of feedstock used and run time. Many gasifier designs produce so much tar that the gas clean up equipment cost is several times the gasifier cost. For the synthesis gas to be used in ethanol production, the level of tar has to be reduced to <50 ppm.

It is known that tar components have an influence on bacteria. A study of Ahmed *et al.* (2006) shows that the presence of tar inhibits the growth of the bacteria *Clostridium carboxidivorans P7T* during synthesis gas fermentation. However, the bacteria are not killed. After an adaptation period the bacteria start growing again. It appears that the bacteria are going to produce more ethanol and less acetic acid. So in this respect tar is even beneficial for the process. The work shows that certain amounts of tar do not cause problems for the synthesis gas fermentation process as long as enough adaptation time is taken into account. Still more research is needed to determine which tar concentrations are acceptable. Conclusion is that a gas cleaning system for removal of tars remains necessary although for synthesis gas fermentation processes this needs not to be so elaborate as for catalytic or for combustion applications.

The choice of the gasifier is mainly based on the gasifier requirements as stated before. The most important requirement is the great variety in feed the gasifier must be able to deal with. In the case of a gasification of bio waste the presence of impurities has to be taken into account. Another important issue in the feedrequirements of the gasifier is the size of the feeding material for the gasifier. For an entrained flow and/or a fixed bed gasifier, a relatively small feed size is necessary. These gasifiers need more elaborate grinding than the other type of gasifiers, although grinding is necessary for all gasifiers.

The gasifier configuration must be as simple as possible, in order to keep maintenance at a low level. Besides that it is desirable to use a technique, which is already proven and in which some experience is required. The gasifier has to be robust in order to be able to work with waste streams which differ in composition in time. The entrained flow and the fixed bed gasifiers are most sensitive for this change in feed compositions. Also quick stop and/or start up is more complicated with entrained flow and fixed bed systems.

Another demand set for the gasifiers is the synthesis gas quality. Because the produced synthesis gas will go to the fermentation unit in order to obtain ethanol, the quality and exact composition of the  $\text{CO-H}_2$  is not very important, although it *is* desirable to obtain a continuous composition of the synthesis gas.

Reviewing all the advantages and disadvantages of the different types of gasifiers, a Circulating Fluidised Bed Gasifier (CFB) seems the best choice:

- CFB has a simple design and requires low maintenance.
- CFB is able to tackle a large range of feed without requiring a strict feed-size.

- CFB can be scaled up to deal with larger amounts of feed.
- CFB has high efficiency because of the circulating ash.
- CFB is relatively easy to stop and start.
- CFB produces synthesis gas of reasonable quality.
- CFB is commercially available and already in use in several plants worldwide.

#### Efficiency of the gasifier

In order to combust the feed that is supplied to the gasifier, there must be a continuous addition of heat in the gasifier. To determine the energy added an energy-balance must be made.

Two losses can be pointed out. The synthesis gas will leave the gasifier with a certain temperature and there will be losses through the walls of the gasifier. The loss through the wall depends on the insulation. This loss depends only on the thickness of the insulation-layer and the choice of insulation-material. Because of the high-temperature at the gasifier-wall, the insulation-layer must be built with two components. Directly at the gasifier-wall, a small layer of ceramic wool (~25 mm) must be positioned. The layer around the ceramic wool, consisting of rock wool will be placed to reduce heat-loss through the wall further. The second energy loss consists of the energy taken out by the synthesis gas. Both losses have to be compensated for by the energy generated in the gasifier, usually by the heat of reaction (combustion of the feed). This means for every ton of feed put into the gasifier, between 32.6% and 39.4% is needed to compensate the losses (Van Kasteren *et al.*, 2005).

## 17.3.3 Gas purification

The major obstacle for the large-scale implementation of biomass gasification is the 'tar problem'. The circulating fluidised bed gasifier typically produces ~10 g/ $M_0^{3}$ . Tars in the synthesis gas give rise to fouling, as they deposit on the walls of the system when the tars, due to cooling, condensate. There are numerous purification processes, but few of them are suitable for our application. The OLGA<sup>3</sup> concept seems to be most promising for this process. This concept reaches highest efficiency, has been tested thoroughly and is commercially available. Besides that, this system is designed especially for this purpose. For thermal tar cracking, high temperatures will have to be reached, which leads to extra loss of energy and therefore lower efficiency. The catalytic tar cracking also seems to be promising, but isn't commercially obtainable yet. Besides that, one of the boundary conditions to the plant is that as few as possible additives are to be used. The catalyst in this concept needs extra care especially as deactivation can be a problem and the higher investment costs.

## 17.3.4 Fermentation

After gasification and gas purification the next process step to produce ethanol is fermentation. Fermentation occurs when bacteria metabolise a material into another one. In this case the cleaned synthesis gas can be converted anaerobically into ethanol. Biological production of chemicals from synthesis gas offers several advantages over catalytic techniques:

- Biological conversion occurs under mild temperatures and pressures, whereas catalytic reactors are operated at high temperatures and pressures.
- The reaction specificity of enzymes is typically higher than that of inorganic catalysts.
- Most biological catalysts are tolerant to sulphur gases, reducing the cost of gas cleanup prior to the conversion step.
- In the fermenter the waste gas shift takes place biologically so preventing the use of a separate shift reactor for adjusting the CO/H<sub>2</sub> ratio.

#### Type of bacteria

Several acetogenic microbes are capable of metabolising synthesis gas into ethanol. Two of the more promising strains are described below. Both are grampositive bacteria, this means they are characterised by having as part of their cell wall structure peptidoglycan as well as polysaccharides and/or teichoic acids. The peptidoglycans are heteropolymers of glycan strands, which are cross-linked through short peptides.<sup>4</sup>

- *Butyribacterium methylotrophicum* (Bredwell *et al.*, 1999): It is a grampositive, motile, rod-shaped anaerobic bacterium, which grows on a wide variety of substrates, including glucose, formate and methanol, H<sub>2</sub> and CO<sub>2</sub>, and CO. The latter two are of interest to us. The products achieved are acetic acid, butyric acid, ethanol and butanol. Production of ethanol and butanol is usually low. When production of ethanol and butanol is increased, butanol is dominant.
- *Clostridium species*: In the case of clostridial fermentation it has been proposed that acetyl-CoA is the central intermediate (Roger, 1986). The first of the clostridium species was isolated from chicken waste and grew well on the components of synthesis gas to produce acetate and ethanol. The first optimisations of this species resulted in an approximate 1:1 ratio of ethanol and acetate under optimal conditions (Vega, 1989). After that the developments of the clostridium species have been many.
  - Clostridium ljungdahlii: It is a gram-positive, motile, rod-shaped anaerobic bacterium, which converts CO, H<sub>2</sub> and CO<sub>2</sub> into a mixture of acetate and ethanol. The ratio of these products can be adjusted by pH. When the pH is lowered to 4 the ratio ethanol: acetate becomes 3:1 (Gaddy and Fayetteville, 1995). Further medium adjustment has reportedly nearly eliminated acetate

production and led to an ethanol concentration of 48 g/L (approximately 1 mol/l) on day 25 when using an optimised medium (Phillips *et al.*, 1993). This means the separation of ethanol from water is feasible.

Clostridium carboxidovorans (P7) (Rajagopalan et al., 2002): P7 is a grampositive, motile, rod-shaped anaerobic bacterium, which converts CO, H<sub>2</sub> and CO<sub>2</sub> into a mixture of acetate, butanol and ethanol. The ratio ethanol: butanol:acetate is 6:3:1 in absence of hydrogen. Further developments are expected to include hydrogen and inhibition of the butanol step.

The clostridium species has the most potential and is best suited for the development of ethanol. From the clostridium species P7 has a lot of potential, but because of the early stages of the development of this bacterium and therefore lack of data, *Clostridium ljungdahlii* is most promising for our goal to produce ethanol from synthesis gas at this moment.

Bacterial fermentation of CO,  $CO_2$  and  $H_2$  to ethanol using *Clostridium ljungdahlii* gives the following equations (Klasson *et al.*, 1993):

- (1)  $6 \text{ CO} + 3 \text{ H}_2\text{O} \Rightarrow \text{C}_2\text{H}_5\text{OH} + 4 \text{ CO}_2$   $\Delta \text{G} = 216 \text{ kJ/mol}$
- (2)  $6 \text{ H}_2 + 2 \text{ CO}_2 \Rightarrow \text{C}_2 \text{H}_5 \text{OH} + 3 \text{ H}_2 \text{O}^2 \Delta \text{G} = -97 \text{ kJ/mol}$

The distinctive feature of the followed pathway of these microorganisms seems to involve the reduction of carbon dioxide to a methyl group and then its combination with a molecule of carbon monoxide and CoA to form acetyl-CoA (Ljungdahl, 1986). This combination of reactions has been designated as the acetyl-CoA pathway (Wood *et al.*, 1986).

After cleaning the synthesis gas, the next part of equipment needed is for fermentation. In this equipment the bacteria must be able to convert synthesis gas into ethanol and after this the product (ethanol) has to be removed from the rest of the stream. For energetic, environmental and economic reasons the rest stream (consisting of nutrients, water and a small amount of ethanol) should be recycled into the reactor. This is schematically shown in Fig. 17.3. Here a gas-sampling vessel disengages the gas from the liquid. At the recycle-bottle port, fresh nutrients are added, the liquid effluent is withdrawn, and the pH is adjusted. Experimental studies have shown that the rate-limiting step in synthesis gas fermentation is typically gas-to-liquid mass transfer. This means when the gas gets easier in the liquid mass transfer in stirred tanks is to increase the agitator's power-to-volume ratio. Increasing the power input increases bubble break-up, thereby increasing the interfacial area available for mass transfer.

However, this approach is not economically feasible for the very large reactors being considered for commercial synthesis gas fermentation, due to excessive power costs. Consequently, alternative bioreactor configurations that may provide more energy-efficient mass transfer are needed. The most interesting option is a monolith reactor.



17.3 Schematic diagram of a trickle bed bioreactor.

#### Monolith reactor

A monolith reactor is columnar and does not require mechanical agitation and thus offers the potential for lower power costs than stirred tanks. A monolith reactor (Fig. 17.4) is a packed bed of channels where the liquid and gaseous phase flow in co/current downwards. High gas and low liquid flow rates are typically used, giving relative low-pressure drops. The cells are immobilised on the wall. This development is promising, but requires a lot of knowledge and equipment and is still in the experimental stage for fermenters (Salim *et al.*, 2008).

#### Distillation unit

The incoming liquid will consist of two main components: water and ethanol. These can be separated in a standard distillation tower. As ethanol will be used as a fuel, the ethanol coming out of the distiller may only contain 7 vol-% water (Thuijl *et al.*, 2003). Therefore, this will be the goal of our distiller. The outgoing stream of water will still contain ethanol. To keep efficiency as high as possible, this stream should be inserted in the fermentation reactor.

#### Recycle

The water stream coming out of the distillation unit still has valuable components in it. To preserve these, this stream is used to be the water stream in the fermentation reactor. Because the reaction of the bacteria is dependent on pH as well as on the quantity of nutrient in the flow this should be kept at highest performance



17.4 Picture of monolith reactor used for Syn gas fermentation (Salim *et al.*, 2008).

levels. This can be done by adding nutrients and controlling the pH of the recycle stream.

Figure 17.5 shows an overview of the total process design and Table 17.2 shows the mass balance for 30 000 ton per year input of wood chips to ethanol plant (Van Kasteren *et al.*, 2005).

Apart from ethanol acetic acid is also produced. An important issue for the whole process is the energy required for the distillation of the ethanol/water mixture.

Table 17.3 shows the energy requirements. The concentration of ethanol, which can be reached is crucial to the efficiency and economics of the process.

At least 3–5 wt% ethanol in water should be reached otherwise the energy requirements to separate the ethanol from the water become too high.

Conclusion is that the feasibility of the process is determined by the ethanol concentration reached. Coskata (www.coskata.com) is trying to solve this problem via the use of a membrane.



17.5 Process scheme biomass to ethanol plant (Van Kasteren et al., 2005).

	Stream	Quantity (kg/hour)	Quantity (ton/year)
IN			
	Wood	4167	31252
	0,	70	525 for combustion
OUT	2		
	Ethanol	1175	8812
			(97% ethanol)
	Solids	117	888 with 75 ash
	H <sub>2</sub> O out	761	5698
	2		(3.1% ethanol, 17% AcOH, 80% H2O)
	Liquid	0.8	6
	Gases 1	2183	16373 mainly CO <sub>2</sub>

Table 17.2 Mass balance of the integrated system

Source: Van Kasteren et al. (2005)

Table 17.3	Energy	balance of	of the	integrated	gasification-	fermentation	system
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Item	Required energy MWth	Produced energy MWth
	Gasification unit	
Drying and grinding		0.5 MWe
Gasification		0.52
Cooler		2.22
	Fermentation unit	
Fermentation		1 MWe
Flash		0.07
	Distillation unit	
Distillation column		6–12
Total electrical energy required (MWe)		1,5

Source: Van Kasteren et al. (2005)

## 17.4 Conclusions and future trends

This chapter shows that alcohol production via synthesis gas is common practice for methanol, but not for higher alcohols. The synthesis gas is however coming from fossil sources (mainly natural gas). A biobased synthesis gas to methanol process is being developed but due to its large scale practice large amounts of biomass will have to be transported to one location. For biobased ethanol processes, the sugar to ethanol route has been proven efficient for sugar cane based inputs. The other biobased inputs are all less efficient. The catalytic routes for ethanol production via synthesis gas are still not efficient enough. Only the route via methanol seems the best up to now. For the bacterial synthesis gas conversion routes into alcohols the proof of principle has been shown. At the same time the conceptual process design work has provided insights in the process bottlenecks and optimal overall system design. Great bottleneck is the relative low maximum achieved alcohol concentrations from the biosynthesis gas conversion route (<5 wt%). Future investigations should focus on the creation of higher alcohol concentrations in the final mixture and/or better separation techniques for alcohol water mixtures. The more efficient alcohol recovery from water–alcohol containing mixtures is essential for the process to be energetic and economically more feasible. Butanol is in this respect much more promising than ethanol since it is easier to separate from water and has higher temperature (i.e.  $50-70^{\circ}$ C) is more interesting since this makes the distilling more efficient (Henstra *et al.*, 2007).

# 17.5 Acknowledgements

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# 17.6 Notes

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- 2. http://www.ott.doe.gov/biofuels/gasification.html
- 3. www.ecn.nl
- 4. www.sciencenet.com.au/grampositivebacteria.htm

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18

# Production of biofuels via hydrothermal conversion

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**Abstract:** The topic of this chapter is hydrothermal conversion of biomass, a thermo-chemical technique especially suitable for conversion of wet biomass streams. The chapter deals with the process chemistry and the product distribution with special attention to de-oxygenation reactions and char formation. Furthermore, the main characteristics of the reaction products are discussed. The chapter shows typical process layouts and gives a brief historical overview of the research and the status of the most important industrial and laboratory scale activities. Finally, a critical view on the status of the technology is offered.

**Key words:** hydrothermal conversion, liquefaction of biomass, hot pressurized water, deoxygenation, char formation.

## 18.1 Introduction

Hydrothermal conversion (short form 'HTC') is a thermo-chemical conversion technique in which sub- or super-critical water is used as a reaction medium and/ or as a solvent. Although principally all biomass can be used as feedstock, wet (biomass and waste) streams are the obvious choice of feeds from an energetic point of view. The proposed operating regime is broad and ranges from 250°C to 450°C and from 80 to 300 bar, and depends on the type of products it is aimed at. HTC can be used for gasification and liquefaction (see Fig. 18.1), catalytically and non-catalytically. By using (noble) metal catalysts, complete conversion of biomass to methane-rich gas can be reached under hydrothermal conditions. At more severe temperatures (500–700°C), hydrogen-rich gas can also be obtained. Gasification in hot compressed water is discussed in Chapter 20 of this book.

In this present chapter, we will focus on hydrothermal liquefaction (short form 'HTL'), the conversion of wet streams into condensed products. Typically, HTL is carried out in sub-critical water (temperature < 374°C). Under these conditions, biomass is converted into various components, which, upon cooling to ambient conditions, constitute three different phases: an aqueous phase (comprising water plus dissolved organics), a hydrophobic phase and a gas phase. Extraction of the hydrophobic reaction product results in a solvent-soluble (oil) and a solvent-insoluble part. Acetone is often used as a solvent. The solvent-insoluble product has a char-like appearance



18.1 HTC process options.

and is solid at room temperature. It is a direct remainder of the feedstock (char formed in the pyrolysis reactions) and a product of secondary reactions of liquid products.<sup>1,2</sup> The hydrophobic product has a considerably lower oxygen content (typically 10–30 wt.%) and, consequently, a higher heating value than the feedstock. A direct application of HTL oil (short form 'HLO') and solids is as a fuel. In this process option, HTL yields hydrophobic organic products that are easy to separate from the water phase and can be fed as fuel in boilers, furnaces or gasifiers.<sup>3,4</sup> After fractionation by suitable solvents, the solvent-soluble fraction (oil) is considered for upgrading to transportation fuel precursors, for example by catalytic hydro-deoxygenation.<sup>5–8</sup>

For detailed overviews on HTL, the reader can refer to Moffatt and Overend,<sup>8</sup> Bouvier *et al.*,<sup>9</sup> Stevens,<sup>10</sup> Solantausta *et al.*,<sup>11</sup> Venderbosch *et al.*<sup>12</sup> and Peterson *et al.*<sup>13</sup>

In this chapter, the process layout, chemistry, product characteristics and product distribution are further detailed. Process development and demonstration activities are described as well as the current research focus. The chapter ends with conclusion and future prospects.

## 18.2 Chemistry, product characteristics and product distribution

The HTL process can be described by the following conceptual equation:

Biomass  $\rightarrow$  Gas + water dissolved organics + solvent soluble hydrophobic organics + solvent insoluble hydrophobic organics + H<sub>2</sub>O [18.1]

The gas consists primarily out of  $CO_2$  (and some CO and  $CH_4$ ), while the aqueous phase contains relatively small oxygenated hydrocarbons. The organics in the hydrophobic phase contain considerably less oxygen than the feedstock, in the order of 10–30 wt.% compared to more than 45% in the original oil. Without separation, the solvent-soluble (e.g. acetone) organics and solvent-insoluble organics define one product phase, sometimes referred to as bio-crude. This product has a thick paste-like appearance. The separated solvent-soluble organics form an oily substance: HLO. Table 18.1 lists selected properties of HLO. Solvent-insoluble organics are solid and char-like at room temperature.

Characteristic	PERC <sup>6,35,38</sup>	LBL <sup>35,38</sup>	HTU® <sup>4,5</sup>	WSS (water solvent-soluble) <sup>1,2</sup>
С	78.9	74–78.5	75–82	60–70
Н	8.5	6.8-8.2	6–8	5–6
0	12.5	13–19	10–20	25–35
HHV <sub>dn/</sub> (MJ/kg)	31	36	33.3	20–27
Viscosity (at 100°C), Pa*s Weight: average	135			
molecular weight	370	400	300	
Specific gravity	1.1			

Reported yields are in the following ranges: gas: 5–15 wt.%; water-dissolved organics: 10–25 wt.%; solvent-soluble hydrophobic organics: 30–60 wt.%; solvent-insoluble hydrophobic organics: 0–30 wt.%; and water: 10–30 wt.%. The residence time is a dominant process parameter with respect to the product distribution. After ca. ten minutes reaction time, the gas, water and water-dissolved organics yields become constant. After that time, a significant part of the oil (solvent-soluble organics) is transferred to solvent-insoluble organics (char).<sup>2</sup> At low residence times (less than five minutes), it is possible to produce only very limited amounts of char-like product, but deoxygenation is then obviously limited. The effect of residence time on the product distribution is visualized in Fig. 18.2.

The chemistry of HTL is complex. Nevertheless, all HTL reactions can be classified according to their mechanism: ionic and free-radical reactions.<sup>14-16</sup> Hydrolysis reactions, a class of decomposition reactions of organics involving breakdown by water, are typical ionic reactions catalyzed with bases or acids. Cellulose and hemicelluloses may be completely hydrolyzed under HTL conditions, while only partial hydrolysis of lignin is possible without a catalyst.<sup>17</sup> It should be realized here that in the biomass structure, hemicellulose is bound partially to lignin as well, complicating the hydrolysis reactions and possibly promoting char formation as well. Complete dissolution (hydrolysis) of woody biomass was, however, recently demonstrated with Na<sub>2</sub>CO<sub>3</sub>.<sup>18</sup> Ionic reactions are accompanied/followed by free radical decomposition reactions. These thermal reactions are favoured over ionic reactions at lower pressures, lower densities (gases) and higher temperatures.<sup>19,20</sup> Susceptibility of biomass constituents towards thermal degradation decreases in the order: hemicelluloses, cellulose, lignin.<sup>21,22</sup> In hot compressed water, thermal reactions tend to produce primary char, similar to the char-forming reactions in pyrolysis. During HTL, two types of char have been identified, viz. primary char and secondary char. Primary char is the residue that remains after conversion of solid biomass particles. Secondary char is the char produced via polymerization reactions of liquid decay products. Both phenol (lignin) and sugar derivatives have been identified as being susceptible



*18.2* Formation of WSS organics (water and solvent-soluble) and WSIS organics (water and insolvent-soluble) during HTL of wood.

towards polymerization, but it may be reasonable to assume that primary char is caused primarily by the lignin and secondary char by the sugar derivatives.<sup>1,18,23</sup> Anyway, these polymerization and polycondensation reactions lead to the increase of the average molecular weight of the oil and eventually lead to the formation of solvent-insoluble components (char). Due to the higher order in the reactants (~2) of these polymerization reactions, polymerization can be reduced by dilution. Na<sub>2</sub>CO<sub>3</sub>, as a catalyst, is known to prevent polymerization reactions and thus char formation, but its effect is more complex than just dilution.<sup>24–26</sup> Appell *et al.*<sup>27</sup> proposed the following biomass liquefaction mechanism with Na<sub>2</sub>CO<sub>3</sub> and CO (CH(OH) is used here as a model component for biomass):

$$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCOONa + CO_2$$
[18.2a]

$$-CH(OH)-CH(OH) \rightarrow -CH=C(OH) \rightarrow -CH_2 -CO - HCOO^-$$
$$+ -CH_2 - CO^- \rightarrow -CH_2 - CH(O^-) \rightarrow + CO_2 - (18.2b)$$

$$--CH_{2}--CH(O^{-})-+H_{2}O \rightarrow --CH_{2}--CH(OH)-+OH^{-}$$
[18.2c]

$$OH^- + 2CO + H_2O \rightarrow HCOO^-$$
 [18.2d]

Although the char yield (primary and secondary) is reduced by using alkalis, their use in HTC also has drawbacks. Alkalis react in the process, and the recovery of sodium or potassium from liquid and solid products could be a complicated and

costly procedure.<sup>2,6</sup> In contrast, heterogeneous catalysts do not react away and are easy to recover. For that reason, Knežević *et al.*<sup>2</sup> studied the influence of a Ru/TiO<sub>2</sub> catalyst on the HTL process. Compared to non-catalytic experiments, they found that the tested catalyst (1) increased the gas yield, (2) decreased the char yield and (3) had a small effect on the oil yield. The lower char yields in catalytic tests suggest that the catalyst was able to convert the solvent-insoluble product (char) into gas. This was confirmed in an independent experiment using the solventinsoluble product of glucose as a feedstock. In this test of 60 minutes at 350°C, ca. 30 wt.% of gas was produced that consists of CO<sub>2</sub> and CH<sub>4</sub>. Without catalyst, under otherwise identical conditions, gas production was only 2–3 wt.%.<sup>1</sup>

Although the exact reaction pathway of HTL is not yet unravelled, at least four reactions have to be incorporated in a lumped (engineering) reaction path model: (1) depolymerization reactions, (2) decay reactions of the monomers (e.g. dehydration: glucose  $\rightarrow$  HMF), (3) reactions causing the formation of gas (CO<sub>2</sub> and/or CO by decarboxylation/decarbonylation), and (4) polymerization/ polycondensation reactions.

Knežević *et al.*<sup>28</sup> visualized the liquefaction of wood in closed quartz capillaries (see Fig. 18.3a). The formation of secondary char from glucose (Fig. 18.3) was also visualized in those capillaries.<sup>1</sup>



18.3 (a) Liquefaction of wood at 340°C.<sup>28</sup> (b) Formation of secondary char from a 7.6 wt.% glucose solution at 350°C.<sup>1</sup>



For a detailed overview of the chemical reactions in hot compressed water, the reader can refer to several reviews.<sup>14–16,29–31</sup>

## 18.2.1 Deoxygenation

Under HTL conditions, deoxygenation can, to a certain extent, be realized without hydrogen. This is often stated as one of the major advantages of this technique, but apparently, the products would be different than those obtained by catalytic hydrotreating. Depending on the operating conditions and the feedstock, oxygen contents of the hydrophobic phases as low as 4–7 wt.% are reported in the literature.<sup>32,33</sup> However, such low oxygen content is rare and the average reported oxygen concentration is 15–20 wt.%. Oxygen removal under the HTC conditions occurs via the following reactions: dehydration, decarboxylation and decarbonylation. CO added to the reactor or formed in the reactions appears largely converted to CO<sub>2</sub> in the water gas shift or reduction reactions. Consequently, the net effect of deoxygenation during the HTC is the CO<sub>2</sub> and H<sub>2</sub>O formation, the first one being favourable from an

energetic point of view. It has been shown that the reactions of mono-sugars in hot compressed water are dominated by dehydration reactions,<sup>1</sup> resulting in significant water production.

## 18.2.2 Role of water

Water under the HTL conditions has different roles. It is a reaction medium and can serve as a distribution medium for homogeneous and heterogeneous catalysts. Moreover, water itself has a catalytic role in various acid- or base-catalyzed processes due to its higher degree of ionization at the increased temperature. The presence of water in some organic reactions (including hydrolysis and decarboxylation reactions) can cause a decrease of the activation energy, thus affecting their kinetics.<sup>15</sup> Water is also directly involved in chemical reactions under the HTC conditions. Next to hydrolysis, water can oxidize some organic species in both the liquid (e.g. alcohols to ketones) and the gaseous phase (e.g. CO to  $CO_2$  in the water-gas shift reaction).

Under HTL conditions, water is a powerful polar organic solvent due to the strong decrease of its dielectric constant with temperature. Water molecules isolate the reaction intermediates and serve as a physical barrier between them (dilution effect, reducing the higher order repolymerization reactions). In this way, the reaction intermediates are stabilized.

## 18.3 Process layout

Figure 18.4 presents a scheme of a typical HTL process. Prior to feeding into the process, biomass is pretreated to ensure that the feedstock has desired properties: rheological properties, water content, degree of fragmentation of biomass components, etc. Feeding biomass water slurries is a particular challenge due to the problems of biomass settling and filtering and blocking of the process lines, particularly for relatively high biomass/water ratios. Heating to the desired temperature in the range of 250-370°C is performed while water is kept in liquid phase by pressure regulation. HTL can convert very wet streams to a gas without paying a huge energetic penalty, if heat exchanging has taken place efficiently. For this, heat exchange between the reactor effluent and the feed stream is essential that requires operation at high pressures to avoid phase transition (see Chapter 20 of this book). The efficiency of the heat exchanger can be high leading to a feed stream outlet temperature of only 50–100°C below the reactor outlet stream. Make-up heat for the reactor has to be supplied externally. In most cases, tubular reactors have been used in continuous installations. Typically, residence times of 10–90 minutes have been applied. In most reported pilot HTC work, the residence time at an elevated temperature was significantly longer than the ca. five minutes for minimal char formation (see chemistry section), resulting in considerable secondary char formation. In pilot plants, the feed stream was heated externally or



18.4 Typical HTL process layout.

by heat exchange with the reactor effluent. For both cases, it holds that the heating trajectory is already taking several minutes because of heat transfer limitations. The only way to heat biomass in less than five minutes is injecting the feed directly into a hot liquid that may have a negative influence on the energy efficiency in case of a very wet feedstock.

The water phase or oil phase can be recycled for use as a solvent and/or as a dilutant. Keeping the concentration of organics low will decrease the char yield. A low concentration of organics can be achieved by using a (very) diluted feedstock, back mixing or by recycling of water (or oil) over the reactor.

Upon cooling the reactor effluent of HTL, three different products, being also three different phases, are present: a hydrophobic organic phase, an aqueous phase with organic compounds dissolved in it and a gas phase, consisting mainly of  $CO_2$ . Separating gases and the water phase is straightforward. The product gas is made available at a high pressure (> 200 bar), and thus, for its application, expensive gas compression can be avoided. No reported results were found on the separation of oil and char.

## 18.4 Process development and demonstration activities

Already in 1944, Berl<sup>34</sup> reported that the biomass could be converted in hot compressed water into a petroleum-like product. In the 1970s and 1980s, the interest in alternative energy sources, such as biomass, was high due to the oil crises. Liquefaction research was started in 1971 by the US Bureau of Mines,<sup>27</sup> with conversion of carbohydrates in hot compressed water in the presence of CO and Na<sub>2</sub>CO<sub>3</sub>. This combination of CO and Na<sub>2</sub>CO<sub>3</sub> was reported in early HTC

developments to produce in-situ hydrogen,<sup>27</sup> but Molton *et al.*<sup>24</sup> showed that the use of CO in combination with alkali only leads to a limited increase in the oil yield.

Early work by the US Bureau of Mines led to the development of an 18 kg wood per hour process development unit (Albany pilot plant).<sup>35</sup> In this installation, Douglas fir was liquefied, first using the product oil itself (the 'Pittsburgh Energy Research Center/PERC process') and later using water (the 'Lawrence Berkeley Laboratories/LBL process') as a carrier (see Fig. 18.5). For the LBL process, slurries, formed from acid pre-hydrolyzed wood chips and water, were used as

(a) Wood flour Syngas Catalyst Gas to solution Ş vent condenser P and incinerator 57 Crude product Blender High Gas fired slurry Plua flow Product Pressure pressure circulating heater reactor cooler letdown pumps pump Recycle blend catalyst Separator 1 (b) Reactor Boiler Water tank Injection tank Flash tank Condenser , sol 482 Let-down valve 2 C.W. Water pump Bottom Condensate Cooler ☆ ☆ Dewatered sludge Separator 2 C.W. Screw pump Gas Distillate Let-down valve 1

18.5 (a) Scheme of the Albany (LBL process) pilot plant.  $^{35}$  (b) Scheme of the STORS process PDU.  $^{46}$
feedstocks. Operating problems led to several process modifications. However, not all issues were completely successfully resolved.<sup>36</sup> This, along with a large number of parameters that needed to be studied,<sup>37</sup> caused a shift to research in a much smaller scale (continuous 1 l autoclave).<sup>37,38</sup>

HTL, using biomass/water slurries of high organic/water ratios, was studied at the University of Arizona<sup>39–41</sup> and the University of Saskatchewan<sup>42–44</sup> by using special feeding systems.

Another important development involved sewage sludge treatment in the so-called sludge-to-oil reactor system (STORS). This process was developed using autoclaves and continuous installation with the capacity of 30kg of concentrated sewage sludge (20 wt.% solids) per hour in the Battelle Pacific Northwest laboratories of the US Department of Energy.<sup>45</sup> Sodium carbonate was employed as a catalyst.

After a period of reduced attention, the interest in conversion of biomass into energy carriers was renewed in the mid-1990s driven by political, environmental and economical incentives. For example, work on the Hydro-Thermal Upgrading  $(HTU^{(B)})$  process, developed during 1980s in the Shell Laboratories in Amsterdam, was restarted using a bench-scale experimental setup (10 kg water-biomass slurry per hour)<sup>5</sup> and a pilot plant (20 kg dry matter per hour).<sup>4</sup> To the best of the authors' knowledge, this plant is now mothballed.

Several demonstration and (semi) commercial activities can be identified as well. A five 5-ton per day STORS process demonstration plant was built in Japan, with the aim of converting sewage sludge into a combustible energy carrier (see Fig. 18.5).<sup>46</sup> After a successful municipal wastewater treatment STORS demo project in Colton, California, ThermoEnergy (USA) has patented the improved wastewater treatment process marketed under the name 'Thermofuel process'. EnerTech Environmental Inc. (USA) is also developing a process for converting sewage sludge into a solid energy carrier, the 'Slurrycarb process'. The company operates a 1-ton per day process development unit, a 20-ton per day process demonstration unit in cooperation with Mitsubishi Corporation in Ube City (Japan), and is currently commissioning a commercial-scale facility in Rialto, California. When completed, the installation will convert more than 880 wet tons of bio-solids per day from five municipalities in the Los Angeles area into approximately 170 tons per day of the product called E-Fuel.

Changing World Technologies was developing a so-called thermodepolymerization and chemical reformer process for conversion of turkey waste (carcasses) to fuel products and fertilizer. The company used a 15-ton per day pilot plant and a 200-ton per day processing unit (the Renewable Environmental Solution unit in Carthage, Missouri).

From this overview, it appears that the HTL of specific feedstocks to hydrophobic fuels for combustion (specifically solids) is nearing commercial operation. On the other hand, application of HTL for broader range of feedstocks and for production of transportation fuel precursors is still in the development stage.

## 18.5 Current research

Next to the pilot plant studies, a significant amount of laboratory-scale research was performed over the last four decades.<sup>23,26,47–52</sup> In the past and also currently, this research has been dominated by chemical and kinetic studies. Mostly, these investigations use model components instead of real biomass. Recently, several complete reviews have appeared on these items.<sup>13,29–31</sup> There is hardly any process development research ongoing. Also, the link between the insights gained by the chemical research with possibilities for process improvement is not well worked out. It is interesting to note that several research groups have realized that the knowledge obtained from HTL research is very useful for the development of other processes such as high-pressure thermal treatment of bio-liquids (HPTT),<sup>53,54</sup> hydrodeoxygenation (HDO)<sup>55–58</sup> and solvolysis.<sup>59,60</sup> In particular, the knowledge of polymerization reactions of biomass' decay products in HTL has provided, and can still further offer, many insights in the mechanisms and problems in HPTT, HDO and solvolysis.

## 18.6 Conclusions and future trends

With HTL, hydrophobic solid and liquid fuels for combustion and gasification can be prepared from biomass/water mixtures or slurries. Formation of a solid/ liquid hydrophobic phase to be used for its heating value does not require a high yield of a low-molecular weight oil fraction suitable for refining. In this case, the basic requirements for hydrophobic product are reasonable transport and storage properties and a sufficiently high heating value. Factors that increase the formation of secondary char, such as high feedstock concentrations, long residence times and unfavourable temperature profiles, are not of primary concern here. Instead, process optimization should focus on maximizing the yield of hydrophobic products from an aqueous feedstock and decreasing the oxygen content of this combined oil-char product. Economics will strongly depend on feedstock cost and selling price of the products. Because it is still a rather complex high-pressure (200 bar) conversion process, which produces a product used only for its combustion value, such HTL process can only be applied to feedstocks, with a very low, or preferably, negative value (waste), to be economically feasible. Therefore, this HTL processing option should focus on handling aqueous biomass/ waste streams. Robust high-pressure feeding pumps and waste water postprocessing are still technical challenges. Although not yet applied on a large scale, several firms are offering such processes based on relatively recent developments, but more demonstration and commercial applications are needed.

HTL aimed at producing useful intermediates for making transportation fuel blends is still in an early stage of development. However, this option could be economically attractive if a product with high(er) added value is made (e.g. a transportation fuel precursor). The high value product, if produced in a significant yield, would even justify the use of dry solid biomass as feedstock, despite the complexity of feeding slurries of dry biomass and addition and recycling of water or product. In order to achieve an attractive process, oxygen should be removed from the biomass feedstock during the process by  $CO_2$  formation, and the production of very heavy components (in char and in oil) should be avoided as much as possible. The processing route towards transportation fuel precursors also has technical challenges and, in addition, needs significant developments in optimizing desired product yields and realizing efficient decrease of the oxygen content for different feedstocks.

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**Abstract:** The production of synthetic fuels from biomass via Fischer-Tropsch (FT), otherwise known as biomass-to-liquids (BTL) process, constitutes one of the most promising routes for tomorrow's fuels. In this chapter, basic topics, as well as current advances in the production of FT biofuels, are discussed. Starting with a short discussion on biomass gasification and syngas conditioning, the main types of FT reactors and catalysts, along with the different technologies for upgrading FT liquids to premium fuels are thoroughly discussed. Closing, recent advances in the commercialization of the BTL process are presented, along with a discussion on the advantages and limitations of this process and its outlook in the future fuels market.

**Key words:** biomass-to-liquids (BTL) process, Fischer-Tropsch (FT) synthesis, biomass gasification, Fischer-Tropsch reactors, upgrading of BTL-FT products.

## 19.1 Introduction

Growing environmental and security of supply concerns are the main drivers that bring about changes to fuel products. European Union (EU) policies on local air quality, climate change and sustainability, applied via Fuel Directives or Emission Directives, have strongly influenced research efforts and advances in conventional fossil, synthetic and bio-origin fuels. These, in combination with the depletion of the crude oil reserves, have rendered the production of hydrocarbons via the Fischer-Tropsch (FT) synthesis as one of the most promising routes for tomorrow's fuels. According to a recent study (Takeshita and Yamaji, 2008), 'FT synfuels become a major alternative energy carrier and have a noticeable share in the global final energy mix regardless of  $CO_2$  policy.'

The production of fuels via FT involves the conversion of the feedstock to synthesis gas (carbon monoxide and hydrogen) and subsequent synthesis of hydrocarbons via the FT synthesis reaction:

$$CO + 2 H_2 \rightarrow \text{'-}CH_2\text{-'} + H_2O$$

$$[1.1]$$

where '-CH<sub>2</sub>-' represents a product consisting mainly of paraffinic hydrocarbons of variable chain length.

Generally, the FT process is operated in the temperature range of 150–300°C to avoid high methane by-product formation. Increased pressure leads to higher conversion rates and also favours the formation of desired long-chain alkanes. Typical pressures are in the range of one to several tens of atmospheres. The FT hydrogenation reaction is catalyzed mainly by Fe and Co catalysts, while the size and distribution of the hydrocarbon products of the reaction is generally governed by the Anderson-Schulz-Flory (ASF) chain polymerization kinetics model (Bartholomew, 1990).

One of the most important advantages of FT is its versatility concerning both feedstock and products. The FT process can produce hydrocarbons of different lengths from syngas originating from any carbon-containing feedstock, such as coal, natural gas and biomass. Depending on the feedstock, the process is referred to as CTL (coal-to-liquids), GTL (gas-to-liquids) or BTL (biomass-to-liquids). Moreover, synthetic fuels have distinct environmental advantages over conventional crude-refined fuels since they are virtually free of sulphur, nitrogen and aromatics. At the same time, they are largely compatible with current vehicles and fully blendable with conventional fuels and can thus be handled by existing fuel infrastructure. However, both the high energy demands and the large capital cost of FT plants contribute to the high price of synthetic FT fuels, and as a consequence, the economic viability of the FT process largely depends on the price of crude oil.

The FT process is not a new concept. It was first developed in Germany in the 1930s, as Germany was very poor in oil resources and needed, during the Second World War, to develop an independent source of transportation fuels based on their abundant coal resources (Davis, 2002). The exploitation of the vast oil reserves of the Middle East after the Second World War made the FT process uneconomical and interest decreased, with the exception of South Africa. South Africa has vast coal deposits, and the high oil prices combined with the oil embargo during the 1970s led to the great development of the FT process from SASOL (South African Synthetic Oil Limited) (Overett et al., 2000). The technical advances in the FT process and the increasing crude oil prices in combination with the depletion of the crude reserves have led, in the last few decades, to a renowned worldwide interest in the FT process. The FT process has already been commercialized on a large scale. Sasol Synfuels currently operates two CTL plants, processing 45 million tonnes of coal per year and fulfilling about 28% of South Africa's diesel and petrol needs (Dry, 2002). Since 1993, Shell in Malaysia (Bintulu) and PetroSA in South Africa (Mossel Bay) have been operating industrial FT synthesis facilities, which produce liquid fuels from synthesis gas that originally comes from natural gas (GTL). Shell is currently constructing a new GTL plant in Qatar, which will be the world's largest plant converting natural gas into 140 000 barrels per day of clean-burning liquid transport fuel and other products (Shell, 2009). A similar plant is also being built by Sasol and Oatar Petroleum in Qatar in the Persian Gulf.

This renewed interest in the FT process during the 1980s and 1990s was initiated based on the depletion of crude reserves, the subsequent increase of the crude oil price and the worldwide existence of much larger reserves of natural gas and coal. Today, global warming and the universal efforts for  $CO_2$  emissions reduction rekindle the interest in FT technology, as high-quality clean biofuels, compatible with existing infrastructure and vehicle technology, can be produced via the FT process using a wide variety of biomass resources. Materials foreseen to be used in the BTL process include wood and forest residues, agricultural residues and by-products, bagasse, lignocellulosic feedstock from processing residues (paper slurry, black liquor, etc.) and energy crops, with wood being the most commonly considered biomass feed.

The use of renewable resources as feedstock, with all associated environmental advantages, undoubtedly gives synthetic fuels a new dynamic. The production of synthetic fuels from biomass comprises of the three basic steps of all FT processes: gasification of the feedstock (in this case biomass) for production of synthesis gas (CO and  $H_2$ ) and gas cleaning/conditioning, FT synthesis for middle distillates production and upgrading of the FT liquids to high-quality fuel products. However, the development of a commercial BTL process is currently hindered by the fact that, in contrast to GTL, for which industrial synthesis gas production processes have been well known and used for several decades, there is at present no industrial unit for biomass gasification in existence. Closest to commercialization is CHOREN, a German-based technology company that has operated a BTL plant, employing their patented biomass gasification process and the Shell SMDS (Shell Middle Distillate Synthesis) FT process.

Research is actively ongoing on all the three steps of the process in an effort to improve the overall efficiency, with special focus on the biomass gasification step and subsequent gas conditioning prior to the FT reactor in order to meet the strict FT gas purification requirements. Several different types of gasification technology [e.g. fixed bed, circulating fluidized bed (CFB), entrained flow gasifiers, etc.] and operation modes have been considered and assessed and will be discussed later in the chapter.

In the next paragraphs, an overview of the basic topics, including current up-to-date advances in the production of biofuels via FT synthesis, will be discussed. Starting with a short discussion on biomass gasification, including types of gasifiers and gas cleaning techniques, we will then thoroughly describe the main types of reactors and catalytic materials currently employed for FT, followed by a comprehensive discussion on the different processes and technologies for the upgrading of the FT liquids to premium fuel products. In Section 19.3, we will give a description of the final BTL fuel products and their properties. Closing, the most recent advances in the commercialization of the BTL process will be presented, along with a discussion on the advantages and limitations of this process and its outlook in the future fuels market.

## 19.2 Biomass-to-liquids-Fischer-Tropsch process technologies and techniques

Notwithstanding the complexity of the FT plants, all XTL (where X = C for coal, G for natural gas or B for biomass) processes consist of the three main sections illustrated in Fig. 19.1: gasification to syngas and gas cleaning/conditioning, FT synthesis reactor and product upgrading section. Variations and different available options for biomass gasification (pressure, use of oxygen, air medium, etc.), type of FT reactor and catalyst and target products lead to large number of possible process configurations to produce FT liquids from biomass (Tijmensen *et al.*, 2002). All concepts, however, can be grouped into two main categories: full conversion FT, aimed at maximizing FT liquids production, and once through FT, with co-firing of the off gas with natural gas in a gas turbine for electricity production, aimed at maximizing energy efficiency.

Several studies have investigated the technical feasibility and economics of the different BTL-FT processes in order to identify the most promising system configurations (Hamelinck *et al.*, 2004; Henrich *et al.*, 2009; Tijmensen *et al.*, 2002; van Vliet *et al.*, 2009). The outcome of these studies is not conclusive as there are large uncertainties concerning technology status and economic values. Although both biomass gasification technologies and syngas conversion technologies are commercially available and have been demonstrated at a commercial scale, there is very limited commercial experience in integrating biomass gasification fuels. There is, in general, a common consensus that R&D efforts should focus on the following key issues: gasifier designs, syngas quality, product selectivity in chemical synthesis and process integration and scale (E4tech, 2008).

The following paragraphs consist of a description of the main processes, reactor types and catalytic materials employed in these three main sections of the BTL-FT process.



19.1 Schematic line-up of the biomass-to-liquids process.

### 19.3 Biomass gasification to syngas

### 19.3.1 Gasifiers

Gasification converts biomass into a gaseous mixture of syngas consisting of hydrogen, carbon monoxide, methane and carbon dioxide. The gasification of biomass is a crucial matter for the application of the BTL process, as BTL-FT technology has not been established mainly due to difficulties in syngas production/ cleaning-up from biomass. Moreover, almost 75% of the investment costs in a BTL plant are in the pre-treatment, gasification and gas cleaning section; therefore, the gasification pressure and medium greatly influence the economy of both gasifier and downstream equipment (Hamelinck et al., 2004). There are many technologies available for syngas production, as presented in Fig. 19.2 (Balat et al., 2009). Biomass gasifiers can be classified as air-blown, oxygen-blown or steam-blown, as atmospheric or pressurized, as slagging or non-slagging, as fixed bed updraft/downdraft, fluidized bed or entrained flow, and as allothermal (indirect heating) or autothermal (direct heating by combustion of part of the feedstock). A detailed description of the biomass gasification technology and the different types of gasifiers is given in Chapter 16 of the present book, which is dedicated to the production of bio-syngas via gasification. Therefore, attention in the present paragraph is paid to the gasification technology suitable for integration in a BTL-FT plant for the production of liquid fuels.

*Fixed bed gasifiers* have a relatively low throughput and therefore for large-scale applications, as in the case of BTL, with very strict requirements concerning the purity of the syngas, are considered unsuitable (Wang *et al.*, 2008). On the basis of



19.2 Types of biomass gasifiers (Ballat et al., 2009).

throughput, complexity, cost and efficiency issues, *circulating fluidised bed (CFB)* (Hamelinck *et al.*, 2004; Tijmensen *et al.*, 2002; Wang *et al.*, 2008; Zhang, in press) and *entrained flow gasifiers* (van der Drift *et al.*, 2004) are very suitable for large-scale syngas production. Examples of CFB gasifiers employed for the gasification of biomass that have reached a certain degree of commercialization are the Lurgi CFB process, the Foster Wheeler gasifier, the VVBGC gasifier constructed under the EU-funded project Chrisgas, the UCG (Ultra Clean Gas) programmed by VTT, etc. (Higman and van der Burgt, 2008). Slagging entrained flow gasifier manufacturers are Shell, Texaco, Krupp-Uhde, Future-Energy (formerly Babcock Borsig Power and Noell), E-gas (formerly Destec and Dow), MHI (Mitsubishi Heavy Industries), Hitachi and CHOREN (formerly UET) (van der Drift *et al.*, 2004).

The biomass gasification technology most close to commercialization for syngas production in a BTL-FT plant is the CHOREN Carbo-V patented biomass gasification process (Fig. 19.3). The process is a good example of the application of entrained flow gasifiers in the BTL process and is being used in the first demonstration, that is 15000 tons per year BTL plant in Freiberg, Germany, coupled with the Shell SMDS FT process (Rudloff, 2005). The CHOREN Carbo-V patented gasification process consists of three stages: low-temperature, high-temperature and endothermic entrained-bed gasification (Rudloff, 2005). During the first stage, the biomass is continuously carbonized through partial oxidation with oxygen at temperatures between 400°C and 500°C, that is, it is broken down to a tar-containing gas (volatile parts) and solid carbon (char). The tar-containing gas is then fed to the high-temperature gasifier, where it is partially oxidized using oxygen as the gasification agent. The heat, which is released as a



*19.3* Choren Carbo-V gasification process (Higman and van der Burgt, 2008).

result of the oxidation process, warms up the carbonization gas to temperatures that exceed the ash melting point of the fuels that have been used, that is 1300°C–1500°C. At these temperatures, any unwanted longer-chain hydrocarbons, for example tar and even methane, are broken down. The gas that is produced primarily consists of carbon monoxide, hydrogen, carbon dioxide and steam. The char from the low-temperature gasifier is cooled, ground down to pulverized fuel and is then blown into the stream of hot gas coming from the combustion chamber in the entrained flow gasifier. A huge amount of heat is absorbed when gasifying the char, and this allows lowering the temperature of the gas to 800°C–900°C in a matter of seconds. This 'chemical quenching' process produces a tar-free gas with a low methane content and high proportions of combustible carbon monoxide and hydrogen.

#### 19.3.2 Syngas cleaning and conditioning

The syngas purification step is the most expensive part of an FT complex. It accounts for 60–70% of the total cost in the case of natural gas (simplest option). This cost rises up to 50% more in the case of coal-based FT process, with additional 50% cost increase in the case of biomass feedstock (Zhang, in press). Syngas cleaning is, therefore, considered the biggest challenge to the commercialization of the BTL process.

The presence of impurities in the syngas produced by the gasification step is inevitable. Syngas contains different kinds of contaminants such as particulates, condensable tars, BTX (benzene, toluene and xylenes), alkali compounds, H<sub>2</sub>S, HCl, NH<sub>3</sub> and HCN. The catalysts employed in the FT reactor for the synthesis of the liquid fuels are notoriously sensitive to such impurities, and especially sulphur and nitrogen compounds, which irreversibly poison FT catalysts. Alkaline metals and tars deposit on catalysts and contaminate the products, while particles cause fouling of the reactor. Therefore, extensive cleaning of the syngas is required prior to entering the FT reactor. Moreover, the concentration of inert gases (i.e.  $CO_2$ , N<sub>2</sub>, CH<sub>4</sub>, etc.) must be approximately less than 15 vol.% (Boerrigter *et al.*, 2004). Indicative syngas specifications for FT synthesis are shown in Table 19.1 (Boerrigter *et al.*, 2004).

The first step in all syngas cleaning configurations considered so far is the removal of BTX and larger hydrocarbons, the tars. BTX should be removed upstream the active carbon filters in the syngas cleaning train, as active carbon adsorbs BTX and would therefore require frequent regeneration, reducing process reliability. Tars normally condensate at the typical FT reactor conditions and foul downstream equipment, coat surfaces and enter pores in filter and sorbents. Therefore, tars should be removed to a concentration below condensation point at the operating pressure of the FT reactor (Hamelinck *et al.*, 2004). Three processes can be used for tar removal. Thermal cracking of tars involves high temperatures, 1000–1200°C, and tars are cracked in the absence of a catalyst with the use of

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Impurity	Specification
H <sub>2</sub> S + COS + CS <sub>2</sub>	< 1 ppmv
NH <sub>3</sub> + HCN	< 1 ppmv
HCI + HBr + HF	< 10 ppbv
Alkali metals (Na + K)	< 10 ppbv
Particles (soot, ash)	'almost completely removed'
Hetero-organic components (incl. S, N, O)	< 1 ppmv

Table 19.1 Maximum allowable concentration of impurities in syngas

Source: Adapted from van der Drift et al., 2004.

steam or oxygen. However, thermal cracking has low thermal efficiency, requires expensive materials and results in the production of large amounts of soot. Catalytic cracking/reforming of tars in the presence of dolomite/olivine, nickelbased catalysts or alkalis (Wang *et al.*, 2008) overcomes these limitations. Still, this technology is not yet proven and costs are increased due to catalyst consumption (Milne *et al.*, 1998). Alternatively, tars can be removed at a low temperature by advanced scrubbing, using a special organic washing liquid ('oil'). Such a system has been developed by ECN, who have patented the OLGA tar removal technology (Boerrigter *et al.*, 2004). It should be mentioned that the use of entrained flow gasifiers removes the need for a tar cracking/removal step as the high gasifier operating temperatures (1300–1500°C) yield a tar-free syngas.

After the removal of the tars, other contaminants can be removed from the syngas by either the conventional 'wet' low temperature or the 'dry' high temperature cleaning. The wet gas cleaning technology is proven and has been well commercialized for large-scale coal gasification systems (Zhang et al., 2007). The general approach involves the quenching of the raw hot gas with water to cool the gas and remove solid particles (e.g. dust, soot, ash) and the volatile alkaline metals (Boerrigter et al., 2004). NH<sub>3</sub> is then removed by a water washer along with halides and H<sub>2</sub>S is removed either by absorption or the Claus process to elementary sulphur. In the final step, the gas passes through a ZnO and active carbon filters, which remove H<sub>2</sub>S and remaining trace impurities and act as guard beds for the FT catalyst. Although proven, this technology has efficiency penalties and requires additional waste-water treatment. Many research efforts have been focused on the development of dry hot syngas cleaning processes, which appear to be potentially more efficient and cleaner than the proven conventional wet technology (Sharma et al., 2010). Hot gas cleaning consists of candle or ceramic filters for removing solid contaminants and sorbents for fluid contaminants, through which the high temperature of the syngas can be maintained, achieving efficiency benefits and lower operational costs. Dry gas cleaning can be especially advantageous when preceding a reformer or shift reactor, as these processes have high inlet temperatures. However, as aforementioned, the performance and

reliability of the filters and sorbents has still to be proven at high temperatures, especially above 400°C, for a commercial implementation of the dry gas cleaning technology. Recent developments and critical review of the different syngas cleaning technologies have been published and can be found in Sharma *et al.* (2008) and Sharma *et al.* (2010).

After the gas cleaning train, the biomass-derived syngas has to be conditioned in order to adjust the  $H_2/CO$  ratio to that required for the FT reactor. Typical conditioning includes steam reforming of methane and light hydrocarbons to CO and  $H_2$  over a nickel catalyst, followed by a water gas shift (WGS) reactor. Finally, as the concentration of inert gases must be kept below 15 vol.% (Boerrigter *et al.*, 2004), CO<sub>2</sub> is removed with amine treating. The purified and conditioned synthesis gas is then compressed to the required pressure and is fed to the FT reactor.

## 19.4 Synthesis of biofuels via Fischer-Tropsch

#### 19.4.1 FT catalysts

The main requirement for a good FT catalyst is high hydrogenation activity in order to catalyze the hydrogenation of CO to higher hydrocarbons. The only metals with sufficiently high hydrogenation activity to warrant application in FT synthesis are four transition metals of the VIII group of the periodic table: Fe, Co, Ni and Ru. Although Ru exhibits the highest hydrogenation activity, its extremely high price and low availability render it unsuitable for large-scale applications such as the FT process. Nickel, on the other hand, is essentially a methanation catalyst, its application leading to the undesired production of large amounts of methane. Therefore, Fe and Co are the only industrially relevant catalysts that are currently commercially used in FT. The choice of catalyst depends primarily on the FT operating mode. Fe-based catalysts are suitable for the high temperature Fischer-Tropsch (HTFT) operating mode that takes place in the 300–350°C temperature range and is used for the production of gasoline and linear low molecular mass olefins. Both Fe and Co catalysts can be used for the low temperature Fischer-Tropsch (LTFT) that operates in the 200–240°C range and produces high molecular mass linear waxes (Dry, 2002). Moreover, the choice of metal also depends on the feedstock used for the FT synthesis. As Fe, unlike Co, catalyzes the WGS reaction, it is usually used for hydrogen-poor synthesis gas, most especially that from coal (~0.7 H<sub>2</sub>/CO molar ratio), to increase via the WGS reaction the hydrogen content of syngas to the optimum  $2 H_{2}/CO$  ratio of the FT reaction. Cobalt is, therefore, the catalyst of choice for GTL processes, using natural gas as feedstock. Whether the catalysts are Fe or Co, FT catalysts are notorious for their sensitivity towards sulphur and their permanent poisoning by sulphur compounds. As aforementioned, syngas requirements for FT synthesis ask for a sulphur content of below 0.05 ppm (Dry, 1990).

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An extensive amount of research has been performed on several aspects of the Fe and Co catalysts, including fundamental, basic and applied research. These efforts include investigation of the effect of promoters, supports, additives, pre-treatments, preparation and generally all chemical and physical properties of the materials in order to increase catalyst activity, enhance selectivity to the desired products, inhibit formation of unwanted products, especially methane, and improve resistance to sulphur poisoning. A summary of improved, modified Fe and Co catalysts employed in industry for the FT process is presented in Table 19.2 (Bartholomew, 1990).

#### Iron catalysts

Iron-based catalysts are used in both LTFT and HTFT process modes. Precipitated iron catalysts, used in fixed bed or slurry reactors for the production of waxes, are prepared by precipitation and have a high surface area. A silica support is commonly used with added alumina to prevent sintering. HTFT catalysts for fluidized bed applications must be more resistant to attrition. Fused iron catalysts, prepared by fusion, satisfy this requirement (Olah and Molnar, 2003). For both types of iron-based catalysts, the basicity of the surface is of vital importance. The probability of chain growth increases with alkali promotion in the order Li, Na, K and Rb (Dry, 2002), as alkalis tend to increase the strength of CO chemisorption and enhance its decomposition to C and O atoms. Due to the high price of Rb, K

Premium product	Catalysts	Reactors	Processes
$C_2 - C_4$ olefins	Fe/K, Fe/Mn, Fe/Mn/ Ce Fe/K/S, Ru/TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> C <sub>x</sub> Fe/C, Mo/C	Slurry, fluid-bed	Synthol, Koelbel, Rheinpreussen- Koppers DowLPG
Gasoline	fused Fe/K Co/ThO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> /Silicalite, Fe/K/ ZSM-5, Co/ZSM-5, Ru/ZSM-5 Fe/Cu/K and ZSM-5	Fluid-bed, fixed- bed, slurry/ fixed-bed	Synthol Gulf, Badger Mobil, One-Stage Mobil, Two-Stage
Diesel fuel	$\begin{array}{l} {\sf Fe/K, Ru/V/TiO_2 Co/} \\ {\sf Zr, Ti \ or \ Cr/Al_2O_3 \ Co/} \\ {\sf Zr/TiO_2 \ Co-Ru/Al_2O_3} \end{array}$	Fixed-bed (low T), slurry-bed (low T)	Sasol-Arge, Gulf- Badger, Sasol Two Stage, Shell Middle Distillate, Eisenlohr/ Gaensslen
Waxes	Fe/K, Fe/Cu/K Co/Zr, Ti or Cr/Al <sub>2</sub> O <sub>3</sub> Co/R/ Al <sub>2</sub> O <sub>3</sub> , Prom. Fe/Ru	Slurry-bed (low T), Fixed-bed (low T)	Mobil (first stage) Shell Middle Distillate (first stage)

Table 19.2	Catalytic systems	used in industry	/ for productio	n of premium	products
by FTS					

Source: Bartholomew, 1990.

is used in practice as a promoter for iron catalysts. Copper is also typically added to enhance the reduction of iron oxide to metallic iron during the catalyst pretreatment step (Adesina, 1996). Under steady-state FT conditions, the Fe catalyst consists of a mixture of iron carbides and re-oxidized  $Fe_3O_4$  phase, active for the WGS reaction (Adesina, 1996).

#### Cobalt catalysts

Cobalt-based catalysts are especially interesting from the commercial point of view due to their rather high activity and selectivity with respect to linear hydrocarbons. Furthermore, they exhibit higher stability, smaller negative effect of water on conversion and higher resistance to attrition in slurry bubble column reactors (Khodakov, 2009). Cobalt catalysts are only used for the LTFT process, as at higher temperatures, excess methane is produced (Dry, 2002). As the cost of cobalt is higher than that of Fe, it is desirable to increase the surface metal exposure, and therefore, Co-based catalysts are mostly supported on high-surface area stable supports such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or SiO<sub>2</sub> (Oukaci et al., 1999). Zeolites have also been studied as supports (Bessell, 1995). According to a review by Iglesia (1997), the use of support-precursor pairs with intermediate interaction strengths and the slow and controlled reduction of impregnated precursors appears to be the most promising route to the synthesis of supported Co catalysts with high Co concentrations and modest dispersions (0.10-0.15). SiO<sub>2</sub> is considered the ideal support for Co FT catalysts, as its high surface area favours high Co dispersion at high Co loadings, while its surface chemistry enables high reduction of  $Co^{3+}$  or  $Co^{2+}$  to  $Co^{0}$  (Dalai and Davis, 2008). The latter is especially important, as metal Co is the active phase for FT and cobalt oxide is reduced at more than 300°C, temperature higher than the LTFT, implying that pre-reduction of the catalyst should take place prior to loading the reactor with consequent increase of cost and complexity. Promotion with small amounts of noble metals, for example Pt, Ru or Re, also enhances the reduction process (Iglesia et al., 1993). Although, in general, cobalt catalysts are less influenced by the presence of promoters than iron-based ones, the presence of noble metals is claimed to increase activity and selectivity to  $C_{5+}$  products via enhancement of the hydrogenolysis of the carbonaceous deposits and thus the cleaning of the catalytic surface (Iglesia et al., 1993).

#### Suitable catalysts for the BTL-FT process

As discussed in the previous paragraphs, Fe and Co are the industrially relevant catalysts that are currently commercially used in FT, with the choice of catalyst depending primarily on the target product (waxes vs. gasoline and olefins) and the feedstock. Cobalt is the catalyst of choice for GTL processes, using natural gas as feedstock and a  $H_2/CO$  syngas molar ratio of 2, while Fe is used for CTL processes

with a low-hydrogen content syngas. Few studies have investigated in depth the type of catalysts suitable for the BTL-FT process, starting from biomass feedstock (Escalona et al., 2009; Jun et al., 2004; Lapidus et al., 1994; van Steen and Clayes, 2008). It is of crucial importance to explore the differences between GTL and CTL on the one hand and BTL on the other, in order to successfully implement the FT reaction in the BTL process. Both configurations currently investigated for the BTL process (full conversion and once through FT, see Section 19.2) require high overall and per pass CO conversion and high C<sub>5+</sub> selectivity. As cobalt is more active than iron, cobalt has been so far used as the catalyst of choice for economic and exergetic evaluations of the BTL process. However, as analysed in an excellent recent review by van Steen (van Steen and Clayes, 2008), it is debatable whether this is truly the optimal choice of catalyst for the BTL process. van Steen argues that although Fe catalysts can operate with a lower hydrogen content syngas such as that from biomass gasification, a WGS reactor after gasification might be required for both cobalt and iron catalysts in order to obtain a good productivity. Since cobalt yields a higher productivity at high conversion levels, it seems to be the catalyst of choice for BTL synthesis of linear, heavier hydrocarbons if clean syngas is available. However, given that biomass syngas contains several poisons for FT catalysts, such as sulphur-, chloride- and nitrogencontaining compounds, and keeping in view the fact that Fe catalysts are reported to be more resistant to sulphur (van Steen and Clayes, 2008) and ammonia poisoning (Koizumi et al., 2004), the financial risk of operating the FT reactor with an iron-based catalyst seems to be lower. In real operation, deviations from design conditions are inevitable and contamination of the syngas entering the FT reactor is possible. In such case, iron catalysts would be less severely affected than the cobalt ones. Even in the case that the catalyst should be replaced, the much lower cost of iron compared to cobalt offers obvious economical advantages.

Wrapping up, both cobalt and iron catalysts should be considered as options for the FT reactor in the BTL process. A number of scenarios for the BTL process should be developed with both type of catalysts, while the overall process design should be coupled with catalyst developments in both cases in order to clearly prove the superiority of the one catalyst system to the other for commercial application.

#### 19.4.2 Reactors and process conditions

Several good reviews have been published in the last decades analysing the fundamentals and comparing different reactors for the FT synthesis (Dry, 1996; Dry, 2002; Geerlings *et al.*, 1999; Guettel and Turek, 2009; Sie and Krishna, 1999). The heterogeneously catalyzed FT reaction is highly exothermic, with the heat released per reacted carbon atom averaging at about 146 kJ (Anderson, 1956), about an order of magnitude higher than heat released in processes typically applied in the oil industry (Sie and Krishna, 1999). Due to this extremely high

exothermicity, the rapid removal of heat is one of the major considerations in the design of FT reactors that have to be able to quickly extract the heat from the catalyst particles in order to avoid catalyst overheating and catalyst deactivation and at the same time maintain good temperature control. Moreover, the reaction usually takes place in a three-phase system, gas (CO,  $H_2$ , steam and gaseous hydrocarbons), liquid hydrocarbons and solid catalysts, thus imposing great demands on the effectiveness of interfacial mass transfer in the reactor (Sie and Krishna, 1999). Last but not the least, the FT process is a capital-intensive process, and therefore, for both economic and logistic reasons, it is only economically favourable on a very large scale. Easy reactor scale-up is therefore a third important requirement when considering a reactor type for the FT process. Three main reactor types, discussed in the following paragraphs, have been commercialized or are thought as promising for industrial applications: multitubular fixed bed reactors, gas/solid fluidized bed reactors and three-phase slurry reactors.

#### Fixed bed reactors

In a multitubular fixed bed reactor, the catalyst particles are packed into narrow tubes, grouped in bundles and enclosed in an outer shell (see Fig. 19.4). The tube bundles are immersed in water, which abstracts the heat and converts to high



19.4 Multitubular fixed bed reactor for FT synthesis (Dry, 2002).

pressure steam. The use of narrow tubes, high syngas velocities and large catalyst particles ensure rapid heat exchange and minimize exothermic temperature rise (Dry, 1996). The increased particle size of the catalyst is also necessary in order to avoid large pressure drops (Sie and Krishna, 1999), a problem encountered with this reactor type. Still, catalytic particles with a large diameter reduce the effectiveness of the material and the overall reaction rate due to intra-particle diffusion limitation.

Overall, the fixed bed reactor choice is easy to operate and scale-up. It can be used over a wide temperature range and the liquid/catalyst separation can be performed easily and at low costs, rendering this reactor type suitable for LTFT. Moreover, in case of syngas contamination with  $H_2S$ , the  $H_2S$  is absorbed by the top catalyst layer and does not affect the rest of the bed; thus, no serious loss of activity occurs (Dry, 1996). On the down side, fixed bed reactors are expensive to construct and the high gas velocities required translate to high gas compression costs for the recycled gas feed. Moreover, it is maintenance and labour intensive and has a long down time due to the costly and time-consuming process of periodical catalyst replacement (Tijmensen *et al.*, 2002).

Recent advances in this type of reactor are the multitubular fixed bed reactors applied in the SMDS process for the conversion of syngas from methane in a heavy, waxy FT product (Eilers *et al.*, 1990; Sie *et al.*, 1991). Shell operates such reactors in its GTL plant in Bintulu, with a capacity of approximately 3000 bbl/day per reactor. This capacity has an order of magnitude higher than previous fixed bed reactors, developed by Lurgi and Ruhrchemie, and is attained due to the specially developed Shell catalyst formulation and reactor design (Geerlings *et al.*, 1999; Sie and Krishna, 1999).

#### Fluidized bed reactors

Fluidized bed reactors are theoretically an excellent reactor type choice for highly exothermic reactions such as the FT reaction. Fluidized bed reactors offer a much higher efficiency in heat exchange, compared to fixed beds, and better temperature control due to the turbulent gas flow and rapid circulation. At the same time, the high gas velocities do not cause any pressure drop issues and smaller catalyst particles can be employed. This translates to high cost reduction due to smaller required heat exchange area, lower gas compression costs and easier construction. Moreover, fluidized beds permit on-line catalyst removal; thus, no down time for catalyst change is necessary as opposed to the fixed bed reactor (Dry, 1996). However, the fluidized bed reactor is only suitable for HTFT, as it can only operate with two phases, solid and gas. If not, liquid and heavy components deposit on the catalyst, leading to solid agglomeration and loss of the fluid phase (Davis, 2002). This means that fluidized bed reactors cannot be used for maximized production of products heavier than gasoline/naphtha (Steynberg *et al.*, 2004). Moreover, according to Geerlings *et al.* (1999), fluidized bed reactors are more

suitable for coal conversion, as opposed to the fixed bed and slurry reactors that operate well in natural gas conversion processes.

Some disadvantages of the fluidized beds are the complexity in operability, difficult separation of the fine catalyst particles from the exhaust gas (imposing significant capital costs for cyclones and oil scrubbers) and erosion problems due to the high linear velocities (Dry, 1996). Moreover,  $H_2S$  contamination of the synthesis gas feed means complete deactivation.

Currently, two types of fluidized bed reactors have been developed and used mainly by Sasol: the CFB and the fixed fluidized bed (FFB). In the CFB reactor, the fine catalyst particles are entrained by high velocity gas stream through a riser reactor. The catalyst is separated from the effluent by cyclones and is returned to the reactor inlet. Due to fluidization problems observed in the CFB reactor, Sasol developed the FFB version, which operates in the bubbling regime and is internally cooled by cooling tubes, as shown in Fig. 19.5b (Sie and Krishna, 1999). The main advantages of the FFB reactor versus the CFB type are the lower construction costs, increased capacity per reactor, less energy required for gas circulation, less catalyst attrition and easier operation and maintenance (Dry, 2002; Sie and Krishna, 1999).



19.5 Fluidized bed reactors for FT synthesis (Dry, 2002).

#### Slurry reactors

Slurry bubble reactors are a version of the fluidized bed reactors, however, in a three-phase system, that is the catalyst is suspended in a liquid through which the feed gas is bubbled as shown in Fig. 19.6. They are therefore employed for LTFT with high molecular mass liquid waxes as the main product, which naturally serves as the liquid phase of the reactor (Dry, 1996). Slurry reactors share many



19.6 Slurry reactor for FT synthesis (Dry, 2002).

of the advantages of the fluidized bed reactors, such as good isothermal operation due to excellent heat transfer both within the slurry and to the cooling system, no intra-particle diffusion limitations as the catalyst particles are small, lower pressure drop and thus lower compression costs and, of course, easier catalyst replacement (Dry, 1996; Geerlings *et al.*, 1999; Tijmensen *et al.*, 2002). The main disadvantage of slurry reactors is the difficult catalyst/wax separation. The removal of wax, but not catalyst, is a critical aspect of bubble column reactor operation. Sasol, which is the main company operating slurry bubble reactors, uses wax/slurry separation considered to be proprietary information, paying special attention to the production of the catalyst and its physical characteristics as well as to the separation processes (Davis, 2002).

The different reactor types discussed above for the FT synthesis reaction all seem to have limitations and advantages. Therefore, there is no universal optimum FT reactor; the choice rather depends on the target product and the process conditions. According to different modelling studies in literature (de Swart *et al.*, 1997; Iglesia *et al.*, 1991), slurry reactors are more suitable for the FT synthesis and result in up to 60% lower capital costs. Shell, on the other hand, operates a multitubular fixed bed reactor and claims that the superior performance of the Shell catalyst invalidates most of the slurry reactor advantages, rendering the fixed bed technology competitive with the current slurry technology (Geerlings *et al.*, 1999). Therefore, FT reaction selection should be based on process conditions and products, aiming at achieving optimized reactor/catalyst combination, based on the physico-chemical characteristics and activity performance of each type of catalyst.

# 19.5 Upgrading of biomass-to-liquids-Fischer-Tropsch products

Summarizing the above, there are at present two catalyst systems available for largescale commercial plants – cobalt-based and iron-based – and two operating modes of the FT process – low and high temperature. The iron catalyst produces gaseous and gasoline range products when operated in the high-temperature range, usually in fluid catalyst bed reactors. In the low-temperature range, both iron and cobalt catalysts produce a large amount of high boiling, waxy products and straight-run diesel and naphtha. The wax is then upgraded to lower boiling range products and normally distilled to yield highly paraffinic, zero sulphur and zero aromatic middle distillate diesel fuels, with naphtha as a co-product. Typical carbon number distribution of HTFT and LTFT products is given in Table 19.3 (de Klerk, 2008).

Description	HTFT (Synthol)	LTFT (Arge)
Carbon number distribution (mass %)	_	-
C <sub>3</sub> –C <sub>4</sub> , LPG	30	10
$\tilde{C_{5}-C_{10}}$ , naphtha	40	19
$C_{11} - C_{22}$ , distillate	16	22
C <sub>22</sub> and heavier	6	46
Aqueous products	8	3
Compound classes	-	_
Paraffins	> 10%	Major product
Olefins	Major product	> 10%
Aromatics	5–10%	< 1%
Oxygenates	5–15 %	5–15%
S- and N-species	None	None
Water	Major by-product	Major by-product

*Table 19.3* The carbon number distribution of high temperature Fischer-Tropsch (HTFT) and low temperature Fischer-Tropsch (LTFT) products, excluding C1–C2 hydrocarbons

Source: de Klerk, 2008.

As the focus of the BTL process, so far, has been to maximize the production of premium BTL-FT fuels, in this section, we will focus on the technologies for upgrading the FT waxes originating from the LTFT process mode to FT diesel and gasoline by hydrocracking and catalytic cracking, respectively. The upgrading of the FT naphtha co-product to gasoline will also be discussed.

## 19.5.1 Hydrocracking of BTL-FT wax to diesel

Although different options have been proposed for the post-treatment and upgrading of the FT waxes (Dancuart *et al.*, 2003; de Klerk, 2007; Dupain *et al.*,

2005), it is generally accepted that hydrocracking is the most effective route to maximize the middle distillate yield and it is currently the applied option. Given the small number of commercial FT plants, little technology has been developed specifically for the refining of the FT wax products. In most commercial sites, standard crude oil refining approaches have been used without taking into account the specific characteristics of the FT wax product compared to conventional refinery streams, such as extra low aromatics content (< 1 wt.%) and virtually zero sulphur (< 5 ppm) (see Table 19.3).

Conventional hydrocracking takes places over a bifunctional catalyst with acid sites to provide isomerization/cracking function and metal sites to provide hydrogenation-dehydrogenation function. Platinum, palladium or bimetallic systems (i.e. NiMo, NiW and CoMo in the sulfided form), supported on oxidic supports (e.g. silica-aluminas and zeolites), are the most commonly used catalysts, operating at high pressures, typically over 10 MPa, and temperatures above 350°C.

In recent years, considerable research is ongoing to investigate the effect of the operating conditions, both experimentally (Calemma et al., 2005, 2010; Rossetti et al., 2009) and computationally (Fernandes and Teles, 2007; Pellegrini et al., 2004), and the catalytic material on the yield and quality of the FT wax hydrocracking products. Concerning the operating conditions, it was found that wax hydrocracking requires milder pressure and temperature, as the paraffinic nature of the wax implies higher availability of hydrogen in the unit (little hydrogen consuming aromatics) and thus suppressed coke formation (de Klerk, 2008). FT wax hydrocracking to middle distillates is favoured at pressures ranging from 3 to 5 MPa and temperatures between 250°C and 300°C (Calemma et al., 2010) and yields a product containing light paraffins up to  $C_{24}$ , as presented in a product sample chromatograph obtained from FT wax hydrocracking experiments performed in Chemical Process Engineering Research Institute (CPERI) (Fig. 19.7). At these conditions, middle distillate yield ( $C_{10}$ - $C_{22}$ ) reaches up to 80–85 wt.% at intermediate conversion levels (~60 wt.%) (Calemma et al., 2010). At higher conversions, a small reduction in the middle distillate yield can be observed, indicating an increase of consecutive hydrocracking reactions leading to lighter products. Still, the consecutive reactions are limited, allowing the reaction to be carried out at high conversions without lowering significantly the middle distillate selectivity (Calemma et al., 2010).

Extensive work has also been conducted by our group as part of the EU-funded IP RENEW project that explored technology routes for the production of BTL fuels (Lappas *et al.*, 2004). More specifically, the operating conditions (temperature, pressure,  $H_2$ /oil ratio) were investigated in experiments with different commercial hydrocracking catalysts in a specially designed hydroprocessing pilot plant unit. Main conclusions were that with all catalysts, hydrocracking temperature appears to play the most important role and influences significantly the product yields, as shown in Fig. 19.8. It was shown that the yields of naphtha and kerosene in the product increase as the temperature increases and so does the conversion.





*19.8* Effect of temperature on product yields in the hydrocracking of BTL-FT wax.

However, the diesel yield is maximized at a certain temperature and then decreases as a result of higher conversions achieved at higher temperatures (RENEW, 2008). Moreover, it was shown that the yield of gasoline and diesel in the product decreases as the  $H_2$ /oil ratio decreases and so does the conversion. The diesel selectivity is also slightly decreased as a result of the decreasing yield and

conversion. Studies by Calemma *et al.* (2010) showed additionally that the composition of FT diesel, specifically the ratio of iso- and n-paraffins, is also influenced by the operating parameters.

The nature of the catalyst also affects significantly the product quality and vield. Experiments performed in CPERI with three different commercial hydrocracking catalysts showed measurable differences in diesel selectivity at isoconversion as a function of the catalytic material (Fig. 19.9) (RENEW, 2008). Catalysts loaded with a noble metal (particularly Pt) were reported to show better performances in terms of selectivity for hydroisomerization and products distribution in comparison with non-noble metals-based catalyst (Archibald *et al.*, 1960; Gibson et al., 1960). Calemma et al. (2001) reported high diesel selectivities obtained over a Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>2</sub> catalyst during hydroprocessing of FT waxes and attributed the observed results to the mild Brönsted acidity, high surface area and pore size distribution of the support. Zhang et al. (2001) also showed that Pt performs better than Ni and Pd supported on tungstated zirconia for the hydroisomerization of the model compound n-hexadecane. The use of hybrid catalysts based on Pt/WO<sub>3</sub>/ZrO<sub>2</sub> with addition of sulphated zirconia, tungstated zirconia or mordenite zeolites was studied by Zhou et al. (2003). According to the authors, hybrid catalysts based on Pt/WO<sub>2</sub>/ZrO<sub>2</sub> provide a promising way to obtain higher activity and selectivity for transportation fuels from FT products. Given the high cost of noble metals, hydroprocessing of FT waxes has also been



*19.9* Product selectivity at isoconversion for different catalytic materials in the hydrocracking of BTL-FT wax.

studied over nickel catalysts (de Haan *et al.*, 2007). de Haan *et al.* (2007) demonstrated the benefit of using non-sulfided nickel catalysts. In conventional hydroprocessing units, catalysts are sulphated to avoid poisoning by the sulphur species in crude oil. However, in the case of the sulphur-free FT waxes, use of a sulfided catalyst implies the continuous addition of sulphur-containing compounds to avoid catalyst deactivation (de Klerk, 2008). Other advantages of developing a non-sulfided catalyst for the hydrocracking of FT waxes are a simplified, less costly and environmentally friendly process (no H<sub>2</sub>S in the tail gas) (de Haan *et al.*, 2007). Nickel supported on a commercial sulfided NiMo catalyst, with diesel selectivities of 73–77% at a conversion of approximately 52% (de Haan *et al.*, 2007).

#### 19.5.2 Fluid catalytic cracking of BTL-FT wax to gasoline

Although hydrocracking yields an appealing spectrum for the production of diesel, it is not an attractive option for gasoline. The relatively low extent of branching achieved in hydrocracking yields a product in the gasoline range with a low octane number. In addition, hydrocracking is considered an expensive process due to the high pressure operation and high hydrogen consumption. The fluid catalytic cracking (FCC) process has been investigated as an interesting option for the cracking of FT waxes aimed at the production of FT gasoline (Dupain *et al.*, 2005, 2006; Lappas, 2007; Lappas and Vasalos, 2006; Lappas *et al.*, 2007; Triantafyllidis *et al.*, 2007).

The FCC process is the most important refinery process mainly for the production of gasoline from heavy petroleum fractions such as atmospheric and vacuum gas oil (VGO). In the FCC unit, the long hydrocarbons are cracked in the 480–540°C temperature range over zeolite catalysts to smaller n- and i-paraffins, n- and i-olefins and aromatics. Conventional FCC feedstocks are relatively aromatic, with a high sulphur and nitrogen content, in contrast to FT waxes that are highly paraffinic with extra low aromatics content (< 1 wt.%) and virtually zero sulphur (< 5 ppm) (see Table 19.3). Both the development, therefore, of new catalyst formulations and optimization of the overall process parameters are very critical to optimize the yield and quality of FCC products from FT waxes.

Lappas *et al.* (2007) compared the crackability of conventional VGO feed and FT wax provided by CHOREN over a typical refinery FCC E-cat. As can be seen in Fig. 19.10, the FT wax is much more crackable than VGO due to the highly paraffinic molecules of wax compared to VGO that contains a significant amount of aromatics. In fact, the cracking rate of the wax molecules was calculated as about 4.2 times faster than that of the VGO molecules. Moreover, coke formation was much less compared to VGO, again due to the paraffinic nature of the feed and the absence of aromatic compounds or coke precursors even at high conversion levels. Very high conversions, over 80 wt.%, can be achieved with conventional



19.10 Comparison of wax and VGO FCC crackability using E-cat.

FCC catalysts at very low catalyst/oil ratios and low temperatures. In Table 19.4, a comparison between the two feeds regarding the product distribution at 70 wt.% conversion is given. The table shows that gasoline (C<sub>5</sub>, 221°C) yield is about the same with both feeds. Gasoline from VGO has, as expected, a higher octane number; however, the research octane number (RON) of the wax gasoline is still acceptable. The RON of the wax gasoline was almost constant and independent of the conversion exactly due to the low aromaticity of this gasoline (Lappas et al., 2004). Dupain et al. (2006) also observed that the cracking of wax to gasoline is a primary reaction with a gasoline selectivity that is independent of conversion level or temperature. Despite the lower RON number, gasoline from the cracking of FT waxes in an FCC unit is very promising due to the low content of aromatics in the product and the extremely low sulphur and nitrogen concentrations, leading to the production of a very clean gasoline. Moreover, it was found that the diesel range LCO product produced from the catalytic cracking of FT waxes is better than the respective produced from the cracking of conventional FCC feedstocks. The degree of branching in the diesel product is

Table 19.4 Comparison of product yields (wt.% on feed) at 70 wt.% conversion from the processing of vacuum gas oil and BTL-FT wax via FCC

	C/O	Gasoline	Coke	Dry	Total $C_3$	Total $C_4$	LCO	RON	MON
Wax-1	0.9	45.6	0.1	0.35	8.1	16.1	21.3	88.5	77.5
VGO	3.05	46.3	4.3	3.00	5.75	9.85	18.4	94.4	83.3

lower than that of the gasoline, improving marginally the cetane number but acting very beneficially for the diesel cloud point and pour point, in addition to the very low sulphur and nitrogen content (Dupain *et al.*, 2006).

The addition of ZSM-5 additive to a conventional E-cat was found to enhance the cracking rate of FT waxes, enhancing the cracking of gasoline range olefins to gas range olefins and especially propene and butene (Dupain et al., 2006). This was attributed to the diffusions of the initially formed smaller olefins in the ZSM-5 pores. The olefins are not able to leave the ZSM-5 pores rapidly enough, and they are thus easily activated and overcracked to gas range olefins (Dupain et al., 2006). Use of pure ZSM-5 resulted in an octane-enhancing effect of the produced gasoline due to the enhanced formation of olefins and aromatics. Triantafyllidis et al. (2007) investigated the potential utilization of various microporous (zeolites H-Y and H-ZSM-5) and mesoporous [amorphous silicaalumina (ASA) and Al-MCM-41] aluminosilicates as catalysts or active matrices in the cracking of FT waxes towards the production of liquid fuels. Focus was placed on the effect of porous and acidic characteristics of the materials on products yields and properties. According to the authors, the type of catalyst plays a significant role in the product selectivities. The percentage conversion of wax, the product yields [gasoline and liquefied petroleum gas (LPG)] and the RON of the produced gasoline are shown in Fig. 19.11 for different investigated microporous and mesoporous catalysts. The behaviour is typical for the two zeolitic catalysts when used in FCC of petroleum fractions, where H-Y zeolite is being utilized as the main active cracking component of the catalyst and ZSM-5 is being used as an additive in small amounts, leading to lower gasoline and higher LPG yields, and usually to higher RON. Similar trends are observed in Fig. 19.11



*19.11* Conversion, product yields (gasoline and LPG) and RON of produced gasoline in the FCC of BTL-FT wax on different microporous and mesoporous catalysts.

for the cracking of FT waxes. One of the main reaction pathways that ZSM-5 catalyzes with higher rates than H-Y is the cracking of paraffins, thus making it very active in the conversion of waxy feedstocks in agreement with the results of Dupain et al. (2006). The 3%-crystalline H-ZSM-5 sample, not diluted with ASA, showed high conversion activity (79 wt.%), very close to that of the diluted catalyst of the crystalline H-ZSM-5. It can thus be suggested that the acid sites present in this sample are much more active for the conversion of wax compared to those of Al-MCM-41 and ASA, although the very low crystallinity H-ZSM-5 sample consists mainly of X-ray diffraction (XRD) amorphous aluminosilicate phase. Figure 19.12 shows the yields (wt.% on feed) of various gasoline components. The data in Fig. 19.12 can also be used for a qualitative comparison of catalytic performance with regard to selectivity towards specific gasoline components, especially in the case of H-Y and H-ZSM-5-based catalysts, which showed a similar percentage conversion of wax (Fig. 19.11). The H-Y-st. catalyst presented a significant selectivity towards the production of branched paraffins (22 wt.% on feed) compared to much lower yields with the rest of the catalysts (3.5-4 wt.%). The increased formation of branched paraffins in gasoline is considered as a major target towards the production of environmentally friendly fuels in accordance with the EU regulations. Olefins were also higher with the H-Y-st. catalyst (15 wt.% on feed) compared to the rest of the catalysts (~12 wt.%), while naphthenes were 1-2 wt.% for all the catalysts. As far as aromatics are concerned, the H-ZSM-5 catalyst led to higher yields compared to the rest of the catalysts. The high RON values of gasoline with the H-ZSM-5 catalyst (~92, see Fig. 19.11) were mainly attributed to the high aromatics content, while in the case of H-Y-st. catalyst, the high RON (~87) was mainly attributed to the relatively high C5-C7 olefins and iso-alkanes yields. The 3%-crystalline



*19.12* Yields (%wt. on feed) of gasoline components in the FCC of BTL-FT wax on different microporous and mesoporous catalysts.

H-ZSM-5 sample showed similar trends with the fully crystalline H-ZSM-5 with regard to the yields of gasoline components, except for the case of aromatics, which are significantly lower with the former sample. Interestingly, the RON of the gasoline produced from the 3%-crystalline H-ZSM-5 sample remained considerably high (84). The yield of aromatics with the Al-MCM-41 sample was very low, but they cannot be compared with those of the rest of the catalysts due to the relatively low percentage conversion of wax with the mesoporous catalytic material.

In general, research has shown that the cracking of highly paraffinic FT waxes under FCC conditions can yield an interesting spectrum of renewable fuels, both in the gasoline and diesel range, by adapting the process parameters and catalyst formulations. Optimization of catalyst's acidic and porosity properties as well as of process parameters is necessary in order to visualize a potential commercialization of the FCC-based upgrading of FT waxes.

## 19.5.3 Upgrading of BTL-FT naphtha to gasoline

Naphtha is produced as a by-product of the BTL-FT process, both straight-run from the FT reactor and as a co-product of the upgrading of the FT wax to middle distillates. BTL-FT naphtha has a low octane number and cannot be used as a gasoline blending component. The two dominant processes that have been considered for upgrading FT naphtha to high-octane gasoline are isomerization and reforming. Given that straight-run FT naphtha contains olefins and oxygenates that are not compatible with commercial reforming or isomerization technologies, a hydrotreating step is first required to convert olefins and oxygenates in the naphtha to paraffins (Gregor and Fullerton, 1989). According to a techno-economic study by Kreutz et al. (2008), the optimum BTL-FT plant configuration in order to maximize the yield of premium diesel and gasoline fuels is to isomerize a portion of the naphtha in order to convert normal paraffins to isoparaffins and boost its octane value and catalytically reform the other fraction to provide some aromatic content to (and further boost the octane value of) the final gasoline blendstock. However, it is still uncertain whether the additional gasoline blending stock value can justify the great capital and operational costs that these upgrading units impose on the BTL-FT process and explains why this option has yet to be considered in commercial operations.

# 19.6 Biomass-to-liquids-Fischer-Tropsch final fuel products

As analysed in detail in the previous section, the BTL-FT process – as any XTL process – can yield a different range of products, ranging from chemicals and gasoline range hydrocarbons to middle distillate range alkanes, based on the FT synthesis reaction operating conditions, choice of catalyst and reactor type. The BTL-FT process has been, however, mainly studied so far with the aim to

maximize the production of diesel range products due to two main reasons: the decisive shift of EU towards a diesel economy and the increasing EU diesel deficit in terms of refining capacity (European Biodiesel Board, 2008). International Energy Agency (IEA) figures presented in Fig. 19.13 clearly show the upward trend of the diesel demand in the EU compared to the downward trend of gasoline consumption. In addition, EU car registration figures show that the majority of new cars purchased are diesel cars (70% of new cars in France, Italy, Belgium are diesel cars) (ACEA, 2008). In this context, interest in the BTL-FT process lays in the production of renewable, high-quality middle distillate fuels via the LTFT synthesis reaction to diesel, naphtha and FT waxes and subsequent upgrading of the FT waxes to premium diesel. With such BTL-FT configuration, BTL naphtha is produced both as a straight-run and as a co-product of the FT wax upgrading. We will, therefore, focus on the properties and combustion characteristics of the two main BTL-FT final fuel products: diesel and naphtha.



19.13 Evolution of diesel and gasoline demand in EU 27 (IEA data).

## 19.6.1 BTL-FT diesel

BTL-FT diesel is a renewable fuel of excellent quality compared to both fossilderived diesel and first-generation biodiesel produced via the transesterification of vegetable oils. BTL-FT synthetic fuel consists mainly of linear paraffinic hydrocarbons with almost zero aromatics and sulphur compounds. The physical properties of BTL diesel presented in Table 19.5 (Rantanen *et al.*, 2005) demonstrate its very high cetane number that can reach up to 75, much higher than conventional diesel. The big advantage of BTL diesel is that it is directly usable in the present day in transportation sector, and furthermore, it may be suitable for future fuel cell vehicles via on-board reforming since it is free of sulphur. It is fully blendable with conventional diesel and compatible with current diesel

Fuel properties	Biodiesel-FAME	BTL-diesel	Fossil diesel (EN 590/2005)
Density @ 15°C (kg/m <sup>3</sup> )	885	770–785	835
Viscosity @ 40°C (mm <sup>2</sup> /s)	4.5	3.2-4.5	3.5
Cetane number	51	73–81	53
Distillation 10 vol.% (°C)	340	260	200
Distillation 90 vol.% (°C)	355	325-330	350
Lower heating value (MJ/kg)	38	43	43
Lower heating value (MJ/I)	34	34	36
Polyaromatics (wt.%)	0	0	8
Oxygen (wt.%)	11	0	0
Sulphur (pmw)	< 10	< 10	< 10

Table 19.5 Typical properties of different bio- and fossil-origin diesel product streams

Source: Adapted from Rantanen et al., 2005.

engines and with common materials used in the tank system and the engine components. This constitutes a great plus, as the fuel can be used today using the current distribution and retail infrastructure.

Due to its bio-origin, the BTL diesel has much lower CO<sub>2</sub> emissions than fossilderived fuels. Moreover, it shows considerably improved emission behaviour. BTL diesel fuels have been tested by Volkswagen AG and DaimlerChrysler AG in modern, state-of-the-art passenger cars, as part of the EU-funded IP RENEW project that explored technology routes for the production of BTL fuels (RENEW, 2008). The vehicles were equipped with different types of exhaust gas aftertreatment system, oxidation catalytic converters (oxycats), which reduce CO and hydrocarbon emissions and are the most common technique in the existing fleet and additional diesel particulate filter (DPF), the after-treatment technology of future diesel passenger cars. The reductions of the different emissions with the BTL diesel compared to conventional diesel are summarized in Table 19.6. Great emission reductions were achieved with no special adaptation of the engine. The BTL diesel causes a significant reduction of CO and hydrocarbon emissions, a medium reduction of particulate emissions and only a slight reduction of NOx (nitrogen oxides) emissions. The next lines of the table present emission reductions with different after-treatment technologies and optimization of the engine operation with special software. It can be generally seen that a further reduction of particulates or a significant reduction of NOx can be realized. In general, the BTL diesel manages to reduce not only CO<sub>2</sub> but also the emissions of most air pollutants. What is also important is that the BTL fuel exhibited at least the same fuel consumption as conventional fuels when compared on an energetic basis (RENEW, 2008). With adapted engines, the improved combustion process could also lead to better efficiency and thus reduced fuel consumption.

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Technology	NOx	PM	со	нс
State-of-the-art, no adaptation	-6%	-30%	-90%	-60%
State-of-the-art, Oxycat, PM opt.	-7%	-44%	-95%	-73%
State of the art, Oxycat, NOx opt.	-35%	-12%	-95%	-73%
State of the art, Oxycat, DPF	-29%	-94%	-92%	-79%
Future dedicated BTL, Oxycat + DPF	-72%	-95%	-59%	-16%

*Table 19.6* Emission reduction factors for BTL-FT diesel fuel and different emission reduction technologies (negative values indicate a reduction of emission)

Source: Adapted from RENEW, 2008.

#### 19.6.2 BTL-FT naphtha

Besides the diesel main product, naphtha, a gasoline fraction of less value is produced as a by-product. Straight-run FT naphtha has a low octane number, is olefinic and has high levels of oxygenates (Gregor and Fullerton, 1989). The chemical composition of two naphtha streams produced via LTFT and HTFT process is summarized in Table 19.7. Currently, the BTL-FT synthetic naphtha is rather sold as a low-cost chemical feedstock and cannot be used as a fuel. Untreated naphtha can also be used as an energy source for the production of heat and power or can be alternatively reformed on-site to synthesis gas and fed to the FT reactor to increase the process yield (Bienert, 2007). In the frame of the EU-funded NICE (New Integrated Combustion System for Future Passenger Car Engines) project, Renault/Regienov and Volkswagen tested naphtha fuels in experimental homogeneous charge compression ignition (HCCI) engines and found significant improvements compared to standard diesel fuel (RENEW, 2008). In this context, although BTL-FT naphtha is not a suitable fuel for conventional engines, it may be advantageous for future power trains like HCCI

Product, wt.%	Low temperature Fischer-Tropsch – LTFT	High temperature Fischer-Tropsch – HTFT
Normal paraffins	57.0	7.7
Branched paraffins	3.0	6.3
Olefins	32.0	65.0
Aromatics	0.0	7.0
Alcohols	7.0	6.0
Ketones	0.6	6.0
Acids	0.4	2.0
	100.0	100.0

Table 19.7 Typical composition of straight-run naphtha from LTFT and HTFT

Source: Adapted from Gregor and Fullerton, 1989.

and combined combustion system (CCS) being even more efficient and having less emissions. It should, however, be mentioned that the requirements for these future engines are not clear for the time being.

Even though the light FT by-product naphtha is not suitable for application as a fuel in its present form and in conventional gasoline engines, it could be upgraded by an additional isomerization or reforming unit to boost its octane number and fulfil the above, as discussed in Section 19.5.3. It should be noted that the production of finished gasoline blendstock is not yet considered because of the added cost and energy expenditures associated with upgrading naphtha to gasoline with the current technology.

## 19.7 Commercial status of the biomass-to-liquids-Fischer-Tropsch processes

Within few years, we have witnessed large steps towards the commercialization of the BTL-FT process. There are several companies active in technology development and commercialization of individual steps in the BTL-FT process sequence. A number of companies have large-scale biomass gasification technologies including Conoco Phillips, Siemens, VTT, TPS, CHOREN, Lurgi, Shell, GE, Kellogg Brown and Root, Prenflo, Advantica BGL, Noell, Winkler and KRW (E4tech, 2008). Additionally, there are companies focusing on the production of fuels from syngas, such as Sasol, Shell, JFE Holdings in Japan (slurry bed FT reactor producing dimethyl ether (DME)), Fuel Frontiers Inc. (ethanol from syngas) and Syntroleum (focus so far on CTL and GTL) (E4tech, 2008).

Very few companies, however, are active in the whole BTL process chain. The most important player in the BTL market is CHOREN, a German-based technology company. With its Carbo-V patented biomass gasification process for converting biomass to syngas, the company partnered with Shell and Volkswagen to construct the first commercial BTL plant in the world based on the Carbo-V gasification process and the Shell SMDS FT process. The CHOREN beta demonstration plant in Freiberg, Germany, has been operating since 2005, with a capacity of 45 MW thermal and 15 000 tons of BTL fuel per year. CHOREN is currently constructing the first commercial BTL plant in Schwedt, Germany, with a capacity of 640 MW thermal and 200 000 tons of BTL fuel per year using these technologies, with fuel production scheduled to start in 2012 (Rudloff, 2005).

The efforts of CHOREN for commercialization of the BTL process are complimented by substantial research activities. CHOREN is participating in the OPTIFUEL demonstration project, a 42-month project funded by the EU with 7.8 million Euros within the 7th Framework Program for Research and Technological Development. The project kicked off in February 2010 and is expected to establish the technical basis for the large-scale production of BTL-FT fuels with a consortium comprising besides CHOREN, the automotive companies Ford, Renault and Volkswagen, CONCAWE, representing the European mineral oil industry, Invensys Process Systems as simulation technology provider, research institutes IFP (France), CERTH (Greece), IIT Delhi (India) and the German project consultant SYNCOM. Performance data from the CHOREN Freiberg demonstration plant will be modelled to identify improvement opportunities compared to the current production processes and to create the technical basis for large-scale BTL production facilities. Using BTL products manufactured in the Freiberg plant, the automotive manufacturers and oil industry will work together to blend the BTL liquids, evaluate their exhaust emissions and explore their potential in current and future engine technologies. In addition, the economic aspects and the potential to reduce energy and greenhouse emissions from all parts of the BTL production process will be evaluated. (OPTIFUEL, 2009).

#### 19.8 Future trends

The production of sustainable second-generation biofuels via the BTL-FT process represents one of the most, if not the most, promising option for large-scale replacement of fossil fuels in the world fuels market. Intensive research efforts in the field, from both academia and industry, have significantly advanced progress and have brought the BTL process one step before commercialization. Of course, there are still limitations, technological challenges and plenty of room for further optimization.

The most important advantages of the BTL process have been mentioned throughout this chapter and can be briefly summarized as follows. First, the BTL process is very versatile concerning both feedstock and products; it can produce hydrocarbons of different lengths from any carbon-containing feedstock such as coal, natural gas and biomass, including any lignocellulosic material such as wood and forest residues, agricultural residues, by-products and bagasse, lignocellulosic feedstock from processing residues (paper slurry, black liquor, etc.). Second, BTL-FT fuels are high-quality products, free of sulphur, nitrogen, aromatics and other contaminants typically found in the fossil fuels. Third, BTL-FT fuels are largely compatible with current vehicles and fully blendable with conventional fuels and can thus be handled by existing fuel infrastructure. The incentives that drive progress in the area of biofuels are primarily environmental, and BTL-FT fuels, as biomass-derived fuels, offer considerable reductions in fossil energy use and exhibit reduced greenhouse gas (GHG) emissions compared to their fossilbased counterparts. This is due to the renewable nature of the biomass feedstock and the CO<sub>2</sub> neutral cycle, that is CO<sub>2</sub> emitted during fuel combustion equals the amount of CO<sub>2</sub> adsorbed for the cultivation of the biomass feedstock. Besides their obvious environmental benefits, there are also various parameters that should also be considered for the environmental benefits of biofuels, such as energy consumption for the production of biofuels, transportation requirements of biomass feedstock, final product, etc. It is thus essential to assess the potential of alternative fuels using a life cycle analysis (LCA) approach, considering the full lifecycle of
biofuels from biomass cultivation through production and distribution to the end users. Several LCA or otherwise known well-to-wheel (WtW) studies have been published examining the lifecycle environmental benefits of BTL-FT diesel (Baitz et al., 2004; CONCAWE-EUCAR-JRC, 2008; Fleming et al., 2006; General Motors Europe, 2002; Henrich et al., 2009; van Vliet et al., 2009; Williams et al., 2009). An LCA study investigating the environmental performance of BTL-FT diesel produced via the CHOREN-Shell technology and compared to fossil diesel showed the clear environmental benefits of BTL-FT in different environmental impact categories (Baitz et al., 2004). More specifically, reductions in the order of 61–91% in GHG emissions, 89–94% in smog formation, 3–29% in eutrophication potential and 5-42% in acidification potential can be achieved with the replacement of fossil diesel with BTL-FT diesel. Moreover, in the JRC-EuCar-CONCAWE WtW study (CONCAWE-EUCAR-JRC, 2008), where the lifecycle energy and GHG balance is examined for a wide number of different fuel routes (including coal-, oil-, gas- and biomass-based fuels), BTL-FT diesel appears to have one of the highest potentials for reducing the emissions of GHG gases, as shown in Fig. 19.14.

The BTL-FT fuels, therefore, consist of a very attractive renewable fuel option. Still, there are a number of drawbacks and technological challenges/limitations that need to be addressed to maximize the benefits of BTL-FT fuels and allow their large-scale commercialization and use. One of the main issues is the large capital costs of BTL-FT conversion and the subsequent high price of BTL-FT fuels compared to their fossil counterparts. According to a recent study by Tijmensen *et al.* (2002), short-term production costs of BTL-FT fuels are estimated to be 14 US\$/GJ compared to current diesel costs of around 5 US\$/GJ, a number that also agrees with the estimations of Hamelinck *et al.* (2004). Investment costs represent 50% of this cost, while the biomass feedstock accounts for 40%



*19.14* LCA performance in fossil energy use and GHG emissions of different biofuels (CONCAWE–EUCAR–JRC, 2008).

of the production cost. Technological advancements, which will improve the energy efficiency of the process and reduction of capital cost due to technological learning and scaling, could reduce costs in the long-term future to approximately 9 US\$/GJ. The number is still higher than that of diesel, but taking into account the uncertainties in oil prices and assumptions in the different studies, the long-term economic perspectives of BTL-FT fuels are not considered unattractive.

Because of the complex technology applied for the production of the BTL-FT fuels, production can only be economic in large-scale facilities. A reasonable BTL plant capacity is more than 1 Mt/year biofuel, similar to the existing commercially operated CTL and GTL plants (Henrich et al., 2009). Such large-scale projects entail the uncertainty of adequate biomass resources to procure enough feedstock to feed plants of such scale. This implies great logistical hurdles and large transportation costs. Several biomass pre-treatment options have been investigated to overcome this issue. The two most promising are torrefaction and fast biomass pyrolysis. Torrefaction is a mild thermal treatment in which CO<sub>2</sub> and H<sub>2</sub>O are evaded and the material is made brittle and very easy to mill. The process is suitable for a wide range of biomass materials and has a high energy efficiency of up to 97%. The torrefied material can be handled and fed to the gasifier within existing coal infrastructure (Bergman et al., 2005). Fast pyrolysis of biomass is a process in which biomass is thermally decomposed to bio-oil, gases and char in an inert atmosphere using high heating rates and short residence times at temperatures of 450-550°C (Antonakou et al., 2006; Bridgwater et al., 1999). In both cases, biomass volume is reduced and energy density is increased, therefore decreasing the high transport costs.

Last, but not the least, the current overall efficiency of the BTL plants is relatively low, ranging between 40% and 45% on a higher heating value (HHV) basis (Hamelinck *et al.*, 2004). Further progress has to be made to develop and improve technologies of biomass feedstock pre-treatment, gasification, syngas purification and oxygen production required by the gasification step in a more economic way to achieve better energy integration and carbon balance. In particular, development will need to examine more closely the choice of gasification technology (e.g. entrained flow vs. fluidized bed) and its design to account for biomass feeding and syngas quality requirements, the gas cooling and cleaning technologies to reliably meet the stringent downstream catalytic process requirements while reducing losses in thermal efficiency and the design of downstream processes and optimization of outputs based on considerations of process efficiency and product values, including catalyst development to produce the required products.

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## Production of biofuels via biomass reforming

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**Abstract:** This chapter describes various technologies for biomass reforming for the production of high-value gases. These gas mixtures can be used for the production of fuels and chemicals or as a product itself (like hydrogen). Both 'wet' and 'dry' biomass conversion technologies are detailed with and without intermediate processing steps. Throughout the chapter, the conversion of biomass via fast pyrolysis and subsequent reforming is highlighted.

**Key words:** biomass, steam reforming, reforming in hot compressed water, pyrolysis oil, gasification.

### 20.1 Introduction

Reforming is a technology to upgrade biomass into tuned gas mixtures. Synthesis gas  $(H_2/CO)$ ,  $H_2/CO_2$  gas and  $CH_4/CO_2$  gas are possible products.

A combination of hydrogen and carbon monoxide can be used for the manufacturing of ethers, alcohols and Fischer-Tropsch products.  $H_2/CO_2$ -rich gas is a feedstock for alcohol production. Hydrogen is an interesting fuel as such. There is also an increasing demand for hydrogen in the current petrochemical industry and it is envisaged that hydrogen will become of paramount importance to make biomass compatible with fossil refinery streams. Methane can be used as a substitute natural gas (SNG) for the grid or in compressed form (CNG) as motor fuel. The reform reactions of biomass (here represented by  $C_6H_{10}O_4$ ) can be described by the following conceptual stoichiometric equations:

$$C_6H_{10}O_4 + 2H_2O \rightarrow 6CO + 7H_2$$
 [20.1]

$$C_6H_{10}O_4 + 2CO_2 \rightarrow 8CO + 5H_2$$
[20.2]

Reaction [20.1] is steam reforming and reaction [20.2] represents dry  $(CO_2)$  reforming. Like for fossil feedstock, both reactions require catalysts. The watergas-shift [20.3] and methanation [20.4] reactions will typically reach equilibrium over reform catalysts.

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$
 [20.3]

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$
 [20.4]

The proposed operating regime for biomass reforming is very broad and ranges from 230°C to 1000°C and 1 bar to 300 bar. Without a catalyst, the reaction

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of biomass and  $H_2O/CO_2$  will yield a typical fuel gas at temperatures below 1000°C:

$$C_6H_{10}O_4 + aH_2O \rightarrow bCO + cH_2 + dCO_2 + eCH_4 + fCxHy + gH_2O + tars \quad [20.5]$$

Next to steam and dry reforming, auto-thermal reforming is also a well-known reaction system:

$$C_6H_{10}O_4 + H_2O + 0.5O_2 \rightarrow 6CO + 6H_2$$
 [20.6]

Gasification and reforming of fossil feedstock have been two separate developments. For biomass feedstock, gasification and reforming processes cannot be distinguished that easily. In this chapter, gasification will be used to denote the non-catalytic processes converting biomass into gas, and reforming will be used for catalytic biomass-to-gas technologies. Biomass can be raw biomass from the fields or biomass-derived products such as pyrolysis oil and aqueous by-products from biological conversion processes. For coal and heavy oil, gasification systems are now in operation and for natural gas, associated gas and naphtha reforming is used. Gasification systems for fossil fuels are thermal processes<sup>1</sup> while fossil fuel reforming uses a catalyst (except for the Exxon and Kellog catalytic coal gasification processes, but these never reached commercial implementation<sup>2</sup>). On the other hand, biomass gasification and biomass reforming have always been interconnected technologies. Reforming activity has been introduced originally inside low-temperature (<900°C) biomass gasifiers to upgrade the product gas catalytically. There have been also attempts to create direct contact between solid biomass and catalysts (e.g. by impregnation), but this is outside the scope of this chapter.<sup>3</sup> It has been attempted to add catalytic active materials to the gasifier and to use dedicated down-stream catalytic reactors to remove hydrocarbons (tars) and to upgrade the fuel gas to synthesis gas or hydrogen. Later, reforming systems have been proposed for liquid biomass streams and for very wet biomass feedstock. To understand the developments in biomass reforming, it is necessary to have some insight in 'reforming of fossil fuel or feedstock' (Section 20.2.1), 'gasification of fossil fuel or feedstock' (Section 20.2.2) and 'biomass gasification' (Section 20.2.3). For this reason we start this chapter with short accounts on these technologies.

As mentioned before, the proposed operating regime for biomass reforming is rather broad. This is mainly because two essentially different chemical processes are considered:

- (1) Steam or dry reforming, using pressures up to 30 bar and temperatures of 350–1000°C. In this process the reactants and products are in the gas/vapor phase.<sup>4</sup>
- (2) Aqueous phase or hot compressed water reforming (hereafter called reforming in hot compressed water).<sup>5</sup> This process uses sub- or super-critical water as reaction medium. Temperatures in the range of 230–700°C are used. The

pressure is chosen in such a way that water is either in the liquid or supercritical state ( $T_c = 274^{\circ}C$ ,  $P_c = 220.6$  bar). A typical operating pressure for temperatures above the critical temperature lies around 250 bar.

Next in this chapter, the chemical thermodynamics of biomass steam reforming (Section 20.3) are introduced. Because most reforming catalysts are designed to obtain chemical equilibrium (there are some recent developments<sup>6</sup> that aim at designing catalysts that produce hydrogen by reforming in hot compressed water under conditions favoring methane thermodynamically), this thermodynamic analysis gives insight in the product distribution that can be obtained at different conditions. The biomass feedstock for reforming (Section 20.4.1) is briefly discussed as well as those bio-refinery concepts and processing schemes that include reforming pyrolysis oil or its fractions (Section 20.4.2).

The heart of this chapter is the description of the ongoing research and status of proposed and tested technologies for reforming of biomass (see Figure 20.1), as summarized in the following sections:

20.5.1 Adding reform catalysts to biomass gasifiers



20.1 Technologies for biomass reforming (only the reactors are shown).

- 20.5.2 Reforming of bio-liquids (e.g., pyrolysis oil and its fractions)
- 20.5.3 Reforming of gases/vapors produced by biomass gasifiers/evaporators.
- 20.5.4 Reforming of very wet biomass streams in hot compressed water.

These technologies will be compared and we will end with conclusions (Section 20.6) including R&D needs to mature these technologies.

### 20.2 Related technologies

### 20.2.1 Reforming of fossil feedstock

Gasification (see next Section 20.2.2 for further information) is used for heavy feedstocks like heavy fuel oil and coal while reforming is used for lighter feedstocks, namely natural gas, associated gas, and naphtha. Steam (and dry) reforming are catalytic processes where commercially nickel on alumina-based catalysts are used. To reach high enough conversions to synthesis gas, the temperature of reactor outlet is approximately 850–1000°C at operating pressures up to 30 bar. The inlet temperature can be significantly lower (~500°C). Excess steam, when compared to the stoichiometric reactions, is used to steer the equilibrium conversion of methane and avoid kinetic carbon deposition. Four essentially different steam reforming processes can be identified, namely:

- (1) One-step or single-step steam reforming: An externally fired tubular reactor is being used over which a temperature gradient is applied to reach full conversion.
- (2) Two-step reforming: Initial pre-reforming of the heavier components in the feedstock towards methane and carbon oxides is done around 350–550°C,<sup>7</sup> which is then followed by a consecutive (higher temperature) reformer.
- (3) Auto-thermal reforming: Next to steam, oxygen is supplied internally to generate heat for the strongly endothermic reforming reactions.
- (4) Partial (catalytic) oxidation: Part of the feedstock is combusted without adding additional steam which generates very low hydrogen over carbon monoxide ratios (<2).

For biomass, the pre-reform reaction looks like:

$$C_6H_{10}O_5 + H_2O \rightarrow 3CO_2 + 3CH_4$$
[20.7]

Since steam reforming catalysts and catalysts used in downstream processes (like for methanol and Fischer-Tropsch production) are very sensitive towards sulfur poisoning, the feedstocks are desulfurized. For a complete and detailed review on steam (and dry) reforming of fossil feedstocks, the reader is referred to Rostrup-Nielsen *et al.*<sup>8</sup>

### 20.2.2 Gasification of fossil feedstock

Already around 1850 there was a considerable coal gasification industry. The Siemens gasifier (1861) and the Winkler gasifier (1926) were successful lowtemperature (<900°C) air blown systems producing fuel gas. In 1938, the Koppers-Totzek entrained flow gasifier came into commercial use. This gasifier produced synthesis gas  $(CO + H_2)$  on continuous basis containing no tars and methane at approximately 1850°C and atmospheric pressure from oxygen-entrained coal. At the end of the 1940s and the early 1950s, Texaco and Shell developed technologies for the production of the synthesis gas by oil gasification. These were entrainedflow reactors with top-mounted burners (atomizers) in the down-flow. Operating pressures and temperatures were up to 80 bar and in the range of  $1250-1500^{\circ}$ C, respectively. Apart from Texaco and Shell, Lurgi also developed oil gasification technology, known as multi-purpose gasification. Nowadays, most oil gasifiers are part of a refinery and are used for poly-generation of power, H<sub>2</sub>, synthesis gas and steam. As a result of the oil crisis of the early 1970s coal gasification was taken up again. It was again Texaco and Shell (together with Krupp-Koppers) who developed entrained-flow high pressure (20 bar to 70 bar) and high temperature (>1300°C) coal gasification. A good and complete review on gasification is given by Higman and Van der Burgt.<sup>1</sup>

### 20.2.3 Biomass gasification

At first biomass gasification was primarily envisioned for heat and power production. Nowadays, the production of liquid fuels and chemicals via synthesis gas is also regarded as an interesting route. The developments in the coal and oil industry have led to three archetype (biomass) gasifiers, viz.: fixed bed, fluid bed and entrained flow. From extensions of these archetypes and combinations of them, several derived systems were developed such as slagging fixed beds, circulating fluid beds, twin reactors (indirect gasifiers), etc.<sup>1</sup> Gasifiers operated below 900°C (low-temperature gasifiers) generate so-called fuel gas including tars. Tars are the Achilles heel of this technology; these poly-cyclic components cause, among other problems, fouling (condensation) in downstream units.<sup>9</sup>

Operation above 1300°C (high-temperature gasifiers) results in synthesis gas. Intermediate gasification temperatures of 900–1300°C are unfavorable because the ashes in the feed become partly molten/partly solid – a situation that is almost impossible to handle in a reactor. Both fuel gas and synthesis gas need cleaning (removal of e.g. S, Cl, and alkalis) before entering a catalytic downstream conversion step. Biomass gasification is basically the same technology as coal and oil gasification, except gasification (reforming) processes for very wet feeds which are developed especially for biomass. Differences are: (i) the oxygen content of biomass, (ii) the differences in ash (mineral) composition and amount, and (iii) the reactivity. The differences in reactivity become clear when analyzing the main

gas-producing step: in coal gasification, gas is produced by the heterogonous reaction of solid carbon with  $H_2O$  and/or  $CO_2$ , while for a solid biomass the majority of the gas comes directly from depolymerization/devolatilization reactions of the feedstock. Complete reviews on biomass gasification and the associated problems are those of Beenackers and Van Swaaij,<sup>10</sup> Maniatis,<sup>11</sup> Knoef,<sup>12</sup> and Stassen *et al.*<sup>9</sup>

### 20.3 Chemical thermodynamics

The thermodynamic calculations are done with a Gibbs free energy minimization model<sup>13</sup> using the predictive Soave-Redlich-Kwong Equation of state to calculate the required fugacity coefficients.<sup>14</sup> In the thermodynamic calculations the non-gasified part of the feedstock remains as solid carbon. Biomass is taken as  $C_6H_{10}O_4$  in these calculations. As mentioned before, a thermodynamic analysis gives good insight in the possible product yields, because most reforming catalysts are actually designed to obtain chemical equilibrium.

Figure 20.2 shows the carbon decomposition boundaries for several steam over carbon rations (S/C = 1, 2, 3) against the background of the phase diagram of water. Operating points located above the carbon boundary lines give thermodynamic coke, while points below do not. Obviously, the absence of thermodynamic coke does not give much information about kinetic coke. On the other hand, if thermodynamics predicts coke, there is bound to be coke in practice. In



*20.2* Thermodynamic carbon deposition boundaries for S/C = 1, 2 and 3. Biomass =  $C_6H_{10}O_4$ .

Figure 20.2, the operating regimes for steam reforming and reforming in hot compressed water are also depicted.

From thermodynamic point of view, steam reforming of biomass can be done without coke formation already for S/C = 1 at temperatures above ~700°C. Reforming below 700°C, thus including pre-reforming toward methane, is certainly free of thermodynamic coke for S/C > 2. Reforming in hot compressed water will produce thermodynamic coke for concentrated feedstock solutions of 50 wt% organics or more (S/C = 1, ~57 wt% organics). Above 450°C feeds of up to 40 wt% organics (S/C = 2, ~40 wt% organics) can be handled. For the whole hot compressed region it holds that feeds below 30 wt% (~ S/C = 3), organics do not produce thermodynamic coke. Dry reforming of biomass (reaction equation [20.2]) always produces thermodynamic coke. To avoid coke formation, dry reforming should be combined with steam reforming.

The carbon distribution of the product gas and the hydrogen yield are depicted in Figure 20.3 for relevant conditions for steam reforming and reforming in hot compressed water. The carbon distribution is given as fraction of the total carbon content of the gas and the hydrogen yield is given as fraction of the maximal amount of hydrogen that can be produced according to:

$$C_6H_{10}O_4 + 8H_2O \rightarrow 6CO_2 + 13H_2$$
 [20.8]

The data for reforming in hot compressed water are given for 250 bar, temperatures between 250°C and 700°C and 10 wt% and 20 wt% organics. More concentrated feeds turned out to be very susceptible to coking in practice; more diluted feeds suffer from a too low energetic efficiency. Steam reforming is evaluated between 500°C and 1000°C, 1 bar and 30 bar for S/C = 1 to 12.

For reforming in hot compressed water it can be seen that thermodynamics dictate a  $CH_4/CO_2$ -rich gas below 400°C while gas mixtures containing  $CH_4$ ,  $CO_2$ , and  $H_2$  are obtained at higher temperatures.  $H_2/CO_2$  gas can be only achieved thermodynamically at high temperature (>600°C) and for unrealistic low reactant concentrations (<2 wt%). There are some attempts reported<sup>6,15</sup> to decrease catalytically the methane formation rate via C–O bond cleavage and hydrogenation by poisoning while maintaining the high rates of C–C bond cleavage and shift for hydrogen production. Gas produced by reforming in hot compressed water typically has a (very) low CO content because of the high water concentration in combination water-gas-shift activity.

At 30 bar, steam pre-reforming (~500°C) creates according to thermodynamics  $CH_4$  and  $CO_2$ , while at 1 bar already quite some hydrogen is produced. Complete methane conversion is obtained at moderate S/C (2–3) for 1 bar at 700°C and for 30 bar 900°C is required. The H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratio can be easily manipulated with the steam over carbon ratio. For typical  $CH_4$  steam reforming conditions (S/C = 3, 30 bar) the gas yields are also presented in Figure 20.3. The differences between  $CH_4$  and biomass can be explained by the fact that biomass contains 'internal' water in its molecular structure:  $C_6H_{10}O_4 = C_6H_2(H_2O)_4$ .



*20.3* Carbon distribution and hydrogen yield of the product gas for relevant steam reforming and reforming in hot compressed water conditions as predicted by thermodynamics. Biomass =  $C_6H_{10}O_4$ . For 30 bar and S/C = 3 also the lines for methane steam reforming are given (dotted lines).

### 20.4 Feedstocks and processes

### 20.4.1 Biomass feedstock for reforming

Solid, liquid, and gaseous biomass can be used for reforming. Solid biomass first has to be gasified or evaporated, liquid biomass can either be first evaporated or processed in the liquid/supercritical phase. Gaseous biomass is handled as such.

Solid biomass (waste) is available from already existing industries (like agriculture, wood production, and first-generation biofuels). It is available in its bulk volume or has been densified using for instance pelletization allowing easier handling. The biomass can then be fed to a gasifier using a screw feeder or a hopper system. To convert solid biomass to a liquid has several advantages over using the solid biomass directly.

- A liquid is produced from bulky solid biomass, which is usually difficult to handle. By eliminating void volume which is inevitably present with solid biomass, the energy volumetric density is significantly increased. This makes trans-shipment and transport, especially over longer distances, much more effective.
- It can be stored in tanks. It is often more stable against biological decomposition and cannot ignite at ambient temperature.
- Liquids are easier to process especially when pressurized conversions are envisaged.

With liquefaction, a solution is being given for effectively utilizing biomass: to bridge the large gap of biomass supply and demand, and to do it in a sustainable way. Biomass is available decentralized (where it is being grown) but processing needs to be done centralized to benefit from the economy of scale. Biomass can be liquefied where the biomass is available and then be transported over long distances (road, water) to central processing units of similar scales as the current petrochemical industry. Besides technical and logistic advantages, this conversion chain will also give incentives for economical development and job creation especially in rural areas.

Fast pyrolysis (see Chapter 14) is a liquefaction technology which seems to be very attractive for handling relative dry biomass streams on a worldwide scale. Fast pyrolysis technology produces pyrolysis oil (or bio-oil) via rapid heating of biomass to approximately 500°C in absence of oxygen. In this way, the biomass is thermally decomposed and produces gases, vapors, and char. The vapors are condensed yielding the pyrolysis oil with a yield up to 70 wt%. The gases can be combusted to supply heat for the process and the char can be used as a fuel or it can directly be recycled back to the land since most minerals and metals are concentrated into it. Pyrolysis oil as such can be reformed directly. Additionally, more water-rich fractions of pyrolysis oil are co-produced within various bio-refinery concepts (see Section 20.4.2) which allows 'milder' reforming than the full oil.

Hydrothermal liquefaction can be used to produce oil from wet biomass streams which is the subject of Chapter 18. Very large quantities of low organic water streams are available (e.g., from municipal, fermentation, digestion waste and in the future from algae) which essentially could be used for reforming at elevated pressures. However, the organic concentration must not be too low (> 10 wt%) for the energetic efficiency of the process. Also bio-gas (CH<sub>4</sub> rich) from anaerobic digestion (Chapter 12) can be used as reformer feed which, after a gas cleanup, is essentially a mixture of CH<sub>4</sub>/CO<sub>2</sub>. Trace components in biomass such as sulfur and chlorine are a serious issue in both reforming and downstream catalytic conversions. Sulfur removal is manageable using commercial technologies, such as adsorption (e.g., ZnO, Ni, etc.) and hydrodesulfurization (HDS). HDS (e.g., Albemarle's NEBULA, BASF, Haldor Topsoe) can bring S levels down to single-digit ppm, but is expensive. High chlorine levels pose a greater challenge. The best option for chlorine, ammonia, and metal contaminants is to use dedicated sorption processes for each contaminant. To summarize, various general and specialized cleanup solutions need to be developed and used, depending on the contaminants in gas and the downstream catalysts.

### 20.4.2 Processing schemes for reforming pyrolysis oil or its fractions

For pyrolysis oil already some refinery schemes have been proposed that include reforming. Pyrolysis oil can in principle be steam-reformed directly via gas phase reforming (pressure 1–30 bar) in a stand alone application. However, more integrated process schemes would allow synergy and more favorable economics for both gas phase and high-pressure (liquid or supercritical) reforming. Three examples are briefly discussed below.

#### Co-reforming of biomass in fossil fuel based reformers

For reducing the net CO<sub>2</sub> emissions of commercial gas (natural and associated) and naphtha reformers and lowering the investment costs and implementation barrier, co-reforming of biomass and a fossil feedstock seems very attractive. Pyrolysis oil (or its fractions) and glycerol (from bio-diesel production via transesterification) are interesting candidates as they can easily be pressurized and are relatively clean feedstocks. Biogas (essentially CH<sub>4</sub> and CO<sub>2</sub>) from digesters could be interesting only if they are available in significant quantities at the location of the reformer. The installation of a dedicated pre-reformer for the bio-feedstock would be desirable for the following reasons: (i) minimal changes have to be made to the existing reformer since a methane and hydrogen-rich gas is being fed instead of the original oxygenated compound. (ii) Since co-reforming is considered, the full amount of steam needed for the reformer can be fed to the pre-reformer. The pre-reformer can then operate on very high S/C ratios which is beneficial for the gas chemical equilibrium and minimizes coke formation for which oxygenated compound have a higher tendency to compared to its fossil counterparts. (iii) Impurities like sulfur in the bio-based feedstock are bound to the pre-reformer catalyst acting as a guard bed for the subsequent reformer. Fossil fuel impurities are removed prior to entering the reformer, but this is often not possible for the bio-feedstock due to its high reactivity. In this way, only the pre-reformer catalyst has to be regenerated



20.4 Conceptual scheme of bio-liquid/natural gas co-reforming.

periodically. A conceptual scheme of bio-liquid co-reforming is given in Figure 20.4.

### Extraction of valuable components

Pyrolysis oil contains a mixture of a lot of chemicals of which certain fractions can be interesting for dedicated applications. An example of such a route is given in Figure 20.5 as proposed by the NREL.<sup>16</sup> Here, pyrolysis oil is phase separated via water addition into an aqueous soluble phase and aqueous insoluble phase (here called pyrolitic lignin) which can be used for the production of phenolic resins. The remaining aqueous rich phase is then steam reformed (gas phase) to produce hydrogen. This phase could alternatively also be reformed at higher pressures in hot compressed water.

### Co-feeding biomass to existing refineries

Feeding pyrolysis oil to an existing refinery could facilitate large scale implementation of the use of second generation bio-fuels.<sup>17</sup> The pyrolysis oil would then be fed to specific sections of a refinery (like FCC and hydrotreating). To allow this, pyrolysis oil would need an upgrading step via (mild) hydrogenation. As a side product of this upgrading step, water-rich organic side streams are being produced which would then, via steam reforming or reforming in hot compressed water, be a source for hydrogen for the refinery and the upgrading itself.



*20.5* Proposed bio-refinery network by NREL which includes the reforming of the aqueous phase of pyrolysis oil. Modified from Czernik *et al.*, 2002.

### 20.5 Description of the ongoing research and status of proposed and tested technologies for biomass reforming

### 20.5.1 Adding reform catalysts to biomass gasifiers

Catalytic biomass gasification research<sup>18</sup> has focused on tar removal and hydrocarbon conversion to  $CO/H_2$ . Dedicated efforts to develop catalysts for biomass gasification is in its infant stages, and the strategy till now has been to use catalysts (i) off the shelf, commercial, not so cheap, methane steam reforming catalysts, (ii) cheaper materials, dolomite based clays, alkalis salts (Na, K,

chlorides). Catalysts are used mostly in fluidized bed reactors, such as bubbling or circulating fluidized beds. Because both the feedstock and the catalyst are solids, the catalyst acts only on the gases and vapors produced. When using a fluidized bed reactor the mechanical strength of the catalyst will be very important, besides activity. Unlike Fluid Catalytic Cracking (FCC) catalysts (also a fluid bed process) where the catalyst is a single structure, steam reforming catalysts have a metal supported on a carrier with promoters which makes the catalyst much more vulnerable for attrition. Tests in a fluidized bed with crushed commercial steam reforming catalysts (Süd Chemie C11-NK and ICI 46-1 S) showed a weight loss due to attrition of 28-33% after 48 hours of testing.<sup>19</sup> Stronger fluidizable steam reforming catalysts have been developed. NREL<sup>19</sup> developed pure (99.5 wt%) alumina and alumina based (≥90 wt%, rest being MgO, SiO<sub>2</sub> and K<sub>2</sub>O) fluidizable supports which had a lower surface area than commercial ones  $(1.4-2.7 \text{ m}^2/\text{g})$ versus 9.7 m<sup>2</sup>/g commercial) but a very low attrition rate (0.01 wt%/h versus 0.41-0.69 wt%/h commercial). Dolomite  $CaMg(CO_2)_2$  has gained the most attention as it is very cheap and easy to apply.<sup>20,21</sup> Although its calcined form can convert tars to a large extent it is more often used as a tar-reducer, a guard material, allowing the usage of more active but also more sensitive catalysts downstream.<sup>22</sup> Dolomite is not able to effectively convert methane and suffers from attrition.<sup>21,23</sup> Olivine<sup>23,24</sup> is much more resistant to attrition than dolomite with a somewhat lower activity for tar destruction.

Nickel on alumina based catalysts have been used in the industry for naphtha and natural gas reforming for many years and it was therefore also logical to test them for biomass gasification applications. Baker et al.<sup>25</sup> employed several Ni-based catalysts in a fluidized bed. They observed rapid deactivation which was ascribed to carbon fouling. The mineral olivine, which mostly contains SiO<sub>4</sub>, Mg and Fe with trace elements of Ni, Ca, Al, and Cr, has been proposed as support for nickel based steam reforming catalysts by Courson et al.<sup>26,27</sup> The mineral has superior strength and a mild catalytic activity of its own. When the calcination temperature for NiO on olivine is varied three different connections can be made: (i) the Ni is freely deposited onto the support ( $\sim 900^{\circ}$ C) (ii) the Ni is strongly linked to the olivine (~1100°C) and (iii) the Ni is integrated in the olivine structure (~1400°C). The Ni-olivine which was calcined at 1100°C was found to be the most active for dry reforming of methane.<sup>27</sup> The catalyst was also tested in a fluidized bed gasifier where it showed a higher tar conversion relative to normal olivine as shown in Table 20.1.<sup>28</sup> However, especially the methane was still present in high amounts. The attrition rate of the Ni-olivine was around 0.025 kg/kg of dry fuel. Glass-ceramic catalysts have been proposed by Felix et al.<sup>29</sup> Via controlled crystallization of a mixed melt (in the case for steam reforming Li2O-Al2O3-SiO2 with 15 wt% NiO and traces of MgO) a very strong material is produced which is claimed to be more resistant to attrition than olivine. Steam reforming of an artificial syngas (vol%: 16 H<sub>2</sub>, 8 CO, 12 CO<sub>2</sub>, 4 CH<sub>4</sub>, 16 H<sub>2</sub>O, 44 N<sub>2</sub> and 600–700 ppmv of naphthalene) resulted in a

ivine

Table 20.1 Results of fluidized bed pilot biomass gasifiers using olivine and Ni-olivine.  $^{\rm 28}$ 

'steady-state' relative conversion of ~70–80% naphthalene and 5–10% methane at 800°C.

To the best of our knowledge, no fluid bed catalyst has been developed which has a similar activity and stability compared to fixed bed catalysts.

The current status of catalysts (natural materials or Ni-based) in biomass gasifiers is that they can lower the tar and the higher hydrocarbon content of the gas, which lowers the load on downstream tar removal and upgrading units. There are, however, still operational problems. Catalyst deactivation, catalyst make-up and fluidization problems still need research attention before these dolomite and olivine catalysts could be effectively employed. In practice, tars and hydrocarbons are actually dealt with predominantly downstream of the gasifier.

# 20.5.2 Reforming of bio-liquids (e.g. pyrolysis oil and its fractions)

The research of gasification/steam reforming of pyrolysis oil was initiated by the National Renewable Energy Laboratory (NREL) in the USA. In the nineties of the twentieth century, NREL published the first results<sup>30</sup> on steam reforming of acetic acid (HAc) and hydroxyacetaldehyde (HAA) with the aim to produce hydrogen. HAc and HAA were chosen as model compounds because they represent a part of the pyrolysis oil, which was identified as a possible renewable biomass chemical and energy carrier. A fixed bed microreactor was used to convert the model compounds using grounded commercial catalysts (G-90C and C18HC from United Catalysts Inc.). The thermal stability of the compounds was given as an indicator for coke formation. Both HAc and HAA were catalytically converted to hydrogen-rich gas at a reactor temperature of ~700°C (for HAA a lower inlet

temperature was chosen) and a steam over carbon ratio  $(S/C) \ge 2$ . Further tests with model compound reforming,<sup>31,32</sup> including the vapors of cellulose, xylan and lignin, spraying of glucose, xylose and sucrose onto a fixed catalytic bed in combination with catalyst screening ultimately led to the first actual reforming of the aqueous soluble phase of pyrolysis oil.<sup>33</sup>

Two commercial naphtha/C2-C3 steam reforming catalysts (UCI G90C and the ICI 46-series) showed very promising results in their ability to convert the aqueous soluble phase of pyrolysis oil with only minor coking at high steam over carbon ratios (20-30).<sup>33</sup> However, an increase of methane concentration during a test could be observed. To feed the aqueous soluble phase of pyrolysis oil, adjustments had to be made to the atomizer system in order to directly add the reactant to the catalytic bed. With the improvement of the feeding system, fixed bed reforming of the aqueous soluble phase of pyrolysis oil was still limited to 3-4 hours of operation due to carbonaceous deposits on the catalyst and in the freeboard.<sup>34</sup> To overcome this run time barrier, the reactor bed was changed from a fixed to a bubbling fluidized bed where the commercial catalyst was grounded to a particle size of 300-500 µm. A different catalyst than the ones used before, namely the naphtha reforming catalyst C11-NK from Süd-Chemie, was now being used. The liquid feed was added to the reactor via an externally water cooled atomizer system which was either vertically or horizontally placed.<sup>16,34</sup> The aqueous pyrolysis oil fraction was reformed in the fluidized bed.

Besides catalyst attrition (5%/day), also some catalyst deactivation was observed leading to a rising methane concentration which leveled off at roughly 2.5 vol%. Additionally, methane co-reforming experiments were done where, at co-reforming conditions, two times less unconverted methane was observed than when only methane was being steam reformed.

Steam reforming of the whole pyrolysis oil was done by Van Rossum *et al.* in a bubbling fluidized bed using both a dedicated<sup>35</sup> and commercial reforming catalyst.<sup>36</sup> Initially, a methane free syngas was being produced but in time the methane content increased till it reached the production level of noncatalytic pyrolysis oil gasification. The catalysts activity was then limited to enhancing the water gas shift reaction, coke/char gasification and some pre-reforming activity for  $C_2$ – $C_3$  hydrocarbons. The catalyst showed, similar to the catalyst used by the NREL, high levels of attrition.

Because the chemical mechanism of steam reforming oxygenated compounds is different<sup>37</sup> than methane and naphtha, many research groups have been trying to develop new catalyst formulations using model compounds of pyrolysis oil and the aqueous phase of pyrolysis oil to produce hydrogen and synthesis gas while minimizing coke formation. The details of these investigations are beyond the scope of this chapter. Interested readers are referred to the following publications: Refs. 38, 39, 40, 41, 42, 43 and 44.

# 20.5.3 Reforming of gases/vapors produced by biomass gasifiers/evaporators

Single reactor concepts for both catalytic biomass gasification and pyrolysis oil steam reforming have, up till now, not been able to produce a clean gas for a long period of time. This is mainly caused by the fact that no catalyst has yet been developed which is both mechanically strong and active for a full product gas conversion or is resistant against the 'heavies' formation (char and coke) which is accompanied with the initial biomass conversion step. To solve these problems, both in biomass gasification as in pyrolysis oil reforming staged systems have been proposed.

#### Downstream gasifiers upgrading/cleaning of the gas

Staged gasification was initiated at the University of Zaragoza by Corella *et al.*<sup>45,46</sup> where two fluidized beds were used, one as the biomass gasifier and the second one as a (non-catalytic and catalytic) tar converter. When using a commercial catalyst, initially a clean gas was being produced. After a period of 1–2 hours of successful operation the catalyst started to lose its activity. The heavy tar content of the product gas was identified as being the cause of this deactivation. The introduction of a guard bed with calcined dolomite showed very promising results where no catalyst deactivation was found for a 48 hours on stream.<sup>20,47</sup> Simell *et al.*<sup>48</sup> were successful in a similar approach where calcined dolomite limestone was used as a guard material with a subsequent monolith catalytic Ni-alumina bed. Although the processes have shown its technical feasibility for hours (up to 100 h) of run time the processes were not developed commercially due to the unfavorable economics of that time.

The Biomass Technology Group B.V.<sup>49</sup> is developing a different approach where the biomass is first pyrolysed (~500°C) after which the gas/vapor mixture is subsequently reformed autothermally with the addition of air. From a temperature of around ~1000°C, the product gas is essentially methane and tar free.

### Staged reforming of bio-liquids

Separation of the primary conversion, namely the evaporation of pyrolysis oil, from the catalytic steam reforming seems to have a few advantages:

- Fixed bed commercial catalysts can be directly used which have been proven to be active and do not need additional mechanical strength for fluidization.
- Pyrolysis oil re-evaporation can be done at a lower temperature than the catalytic conversion to syngas, which is beneficial to the overall exergy efficiency of the process.

- Primary pyrolysis oil conversion seems to be mainly thermally driven, followed by catalytic gas upgrading. Actual splitting of these two processes makes separate optimization possible.
- Formed carbonaceous deposits and particles and other impurities like residual ash can be separated before the catalytic fixed bed, making energy utilization possible by burning the carbon or allowing them to gasify using steam and or CO<sub>2</sub>.

The first staged conversion of pyrolysis oil was reported and tested by Van Rossum *et al.*<sup>4,35</sup> where a methane free and low tar syngas was produced at ~810°C and a S/C of 1.5 (see Figure 20.6). Here an 'inert' fluidized sand bed was used followed by a fixed bed with a commercial catalyst. Other proposed and/or tested staged systems include the usage of a pre-catalyst (dolomite,<sup>50</sup> char gasification enhancing,<sup>51</sup>), 'inert' gasification coupled with a current-enhanced catalytic reforming system<sup>52</sup> and a pre-oxidation step to facilitate reforming.<sup>53</sup>

# 20.5.4 Reforming of very wet biomass streams in hot compressed water

Biomass reforming in hot compressed water ( $T = 230-700^{\circ}$ C, pressure high enough to keep water in the liquid/supercritical phase) can convert very wet streams to a gas<sup>5,36</sup> without paying a huge energetic penalty for water evaporation. To achieve this, heat exchange between the reactor effluent and the feed stream is essential which requires operation at high pressures.<sup>54</sup> Figure 20.7 shows a



20.6 Experimental results of fluidized bed pyrolysis oil evaporation/ gasification followed by fixed bed reforming. S/C = 1.5, T (both reactors) ~ 800 °C, hydrogen yield = 68%, carbon to gas conversion = 85%. Modified from Van Rossum *et al.*, 2007 [35].



20.7 Conceptual flow sheet for reforming in hot compressed water.

conceptual flow sheet of such a process. The efficiency of the heat exchanger is high leading to a feed stream outlet temperature of only 100–150°C below the reactor outlet stream.<sup>55</sup> Make-up heat for the reactor can be delivered by e.g. burning of a part of the product gas or exothermic reaction heat in case of methanation. Further promises of the technology are: (i) the product gas is available at high pressure (>200 bar) and thus, for its application, expensive gas compression can be avoided, (ii) the product gas is clean; minerals, metals, and the undesired gases like  $CO_2$ ,  $H_2S$ , and  $NH_3$  (which have a high solubility in compressed water) remain in the water phase and can thus be separated and recovered, (iii) the product gas is not diluted with inert gas, (iv) sequestration of (pure)  $CO_2$  seems readily possible.

These promises however go together with a series of problems that need to be solved in the process development. Pumping of biomass slurries to pressures of up to 300 bar is a challenge. The high temperatures and pressures involved put serious demands on the construction materials to be used, especially because corrosion problems are expected. Here separation of functionalities might be a solution: one material to withstand the pressure and another one for the temperature. Heat exchange between the reactor feed and effluent is required to make the process efficient, but heating of biomass slurry is likely to cause fouling and plugging as the biomass starts to decompose already around 200°C. Catalysts, if employed, need to operate under severe and fouling conditions. However, hot compressed water is a good solvent for most organic chemicals and thus especially useful to keep coke precursors dissolved. Ash deposits will cause problems, and an effective ash removal system must therefore be part of the process. At the time of writing several pilot plants are in operation to facilitate the process development. These pilot plants are still moderate in size: maximally 100 kg/hr wet feedstock.

Without catalysis the process suffers from incomplete conversion and an uncontrollable gas distribution.<sup>5</sup> Catalysis research for reforming in hot compressed water is discussed below for low (230–400°C) and high (400–700°C) temperature separately. Reviews on reforming of biomass in hot compressed water are those by Matsumura.<sup>5</sup> Van Rossum,<sup>36</sup> Elliott,<sup>55</sup> Peterson,<sup>56</sup> Kruze and co-workers.<sup>57</sup>

#### Low-temperature reforming in hot compressed water

Non-catalytic conversion of biomass under these conditions  $(230-400^{\circ}C)$  is very susceptible to the formation of carbonaceous deposits (see also Figure 20.2). In fact without a catalyst, the product distribution consists only for ca. 10 wt% of permanent gases (primarily CO<sub>2</sub>) and 90 wt% condensed products. This is mainly caused by sugars and their decay products as they can easily polymerize in hot compressed water.<sup>58</sup> Pacific Northwest National Laboratory (US) developed a catalytic process for the destruction of organic waste at ca. 350°C while producing a methane rich gas.<sup>59-61</sup> Tests were carried out at laboratory and pilot scale focusing on both catalyst and process development. Ruthenium on rutile titania, ruthenium on carbon and stabilized nickel catalysts showed the highest activity and the best stability. With these catalysts, nearly 100% gasification of model components (1-10 wt% organics in water) was achieved. The gas produced consisted of nearly only  $CH_4$  and  $CO_2$ , as dictated by the overall thermodynamic equilibrium. The catalytic process was carried out in a series of fixed bed reactors. When using feedstock materials with the tendency to produce char/coke, a continuous stirred-tank reactor (CSTR) was required before the fixed bed to soften the feed and to prevent the buildup of solids. Pilot plant runs using complex feeds like potato waste and manure were carried out. The required liquid hourly space velocity (LHSV) was in the range of 1.5–3.5 Nm<sup>3</sup><sub>feed</sub>/m<sup>3</sup><sub>cat</sub>/h. For a waste disposal process these LHSVs are acceptable, but for the production of gaseous energy carriers from biomass the activity is rather low. Waldner<sup>62</sup> reported high extents of gasification and equilibrium methane yield of concentrated (up to 30 wt%) wood sawdust slurries using Raney Nickel as catalyst at 400°C. For complete gasification, 90 minutes reaction time was required in their batch reactor.

The catalysts employed accelerate the rate of the gasification reaction relative to the rate of poly condensation/polymerization reactions, or they are able to gasify the formed polymers, or a combination of both. However, after comparing reaction rates it can be argued that the majority of the gas is produced via gasification of partially polymerized components: in non-catalytic experiments with monomer sugars as feed maximal oil (polymerized components) yields are obtained for reaction times of 2–5 minutes,<sup>58</sup> whereas in catalytic test 30 up to 90 minutes reaction time<sup>62</sup> are needed to achieve complete gasification. Van Rossum *et al.*<sup>36</sup> proposed a simplified lumped reaction path scheme for the conversion of small carbohydrates ( $\leq C_6$ ) in hot compressed water (see Figure 20.8). Savage<sup>63</sup> and Kruze<sup>57</sup> reported extensive reviews on catalysis and reactions in supercritical water.

Huber *et al.*<sup>15</sup> and Cortright *et al.*<sup>6</sup> reported interesting catalysis around 230°C for the production of hydrogen rich gas from small oxygenated hydrocarbons. They were able to decrease the methane formation rate via C-O bond cleavage and methanization (hydrogenation) while maintaining the high rates of C-C bond cleavage and shift for hydrogen production. Cortright used a Pt catalyst, Huber a Raney nickel catalyst promoted with tin. High hydrogen yields were obtained for methanol, ethylene glycol and glycerol. However, with sorbitol and glucose as feedstock already significant amount of methane were being produced next to hydrogen production seems promising to produce hydrogen rich gas at conditions for which overall chemical equilibrium dictates a methane rich gas, viz. at sub critical temperature and at the combination of high temperature and high concentration of organics. In this concept, it will be important to decrease



*20.8* Simplified reaction path scheme for the gasification of small carbohydrates in hot compressed water. All paths can be catalytic or non-catalytic. Im: intermediate component(s).

homogeneous reactions to undesired by-products (oil/char/ $CH_4$ ) and to increase the reaction rate. This is quite a challenge for both catalyst and reactor design.

#### High-temperature reforming in supercritical water

For high temperatures (>500°C), alkalis have been proposed as catalysts.<sup>18</sup> Alkalis promote the water gas shift and methanation reactions leading to more hydrogen or methane production and a carbon monoxide lean gas. The studies on whether or not alkalis enhance the extent of gasification are contradictory.<sup>64,65</sup> Recovery of alkalis from the process may be a problem, because alkalis hardly dissolve in supercritical water. Antal *et al.*<sup>66</sup> reported that leading the effluent of their empty tube reactor over a fixed bed of activated carbon derived from coconut increased the extent of gasification of glucose (1–17 wt% solutions) at 600°C and approximately 60 seconds residence time. The produced gas was at chemical equilibrium. The reaction is much faster at 600°C compared to 350°C, which is beneficial for the size of the reactor. However, no information is yet available concerning the stability of catalysts in the high temperature range supercritical water.

Reported problems with respect to the catalysts are poisoning through trace components such as sulfur, magnesium, calcium and the growth of the active metal crystals during operation (sintering). A general problem of the near and super critical region is that it enhances leaching of the catalytic active phases and degeneration of the support. Furthermore, if coke is formed on the surface of the catalysts, the high  $H_2O$  concentration helps in keeping it clean via gasification. In accordance with that it was found that coke formation on the catalyst surface is a minor problem.<sup>67</sup>

### 20.6 Conclusions

Biomass can be converted via reforming into synthesis gas,  $H_2/CO_2$  gas, and  $CH_4/CO_2$  gas. The technology is in the R&D stage with some pilot work ongoing.

Applying natural catalytic materials (dolomite, olivine) in biomass gasifiers can lower the tar and the higher hydrocarbon content of the gas, thus reducing the load on downstream tar removal and reforming units. Engineered catalysts (primarily Nickel based) for inside gasifiers seem to be a dead end as there are too strong cooking, attrition, and poisoning issues. Tars and hydrocarbons can be removed downstream of the gasifier in relatively standard fixed bed type reformers. It is however essential that the feed gas of the reformer is cleaned from e.g. S, Cl and tertiary tars. Another great challenge will be dealing with the impurities in synthesis gas made from biomass for upgrading in secondary conversions (FT, alcohols, etc.). Downstream upgrading of bio-based fuel gas is technologically feasible (e.g. see the Sasol process for coal gas), but an expensive alternative (e.g. cleaning and pressurization).

Bio-liquids such as pyrolysis oil and its fractions and aqueous waste streams from other (biological) biomass conversions are considered as interesting feedstocks for reforming. These liquids are easy and cheap to pressurize and contain less contaminants than raw biomass. Besides these technical advantages. bio-liquids support a logistic scheme in which the primary conversion can be performed near the source of the biomass feedstock (e.g., remote, rural areas), with large-scale production of the finished bio-fuels in refineries near the market. Reforming of bio-liquids can become an important element of bio-refineries for hydrogen production. For quick introduction and growth of large amounts of bio-fuels, it is essential to integrate and to partner with existing industries and markets. In case of reforming, this can be done by co-feeding natural gas and naphtha reformers with bio-liquids. Reforming of bio-liquids can be done in the gas/vapor phase, the liquid phase or in the supercritical phase. All technologies have potential, but there are still challenges ahead. Optimal process and reactor configurations still have to be developed. Important issues here are handling of coke formation, mineral deposition, catalyst make up, heat addition, and biomass feeding systems. For reforming in hot compressed water feeding of biomass slurries is a real challenge while for the vapor phase system controlled atomization still requires R&D. Dedicated catalyst systems will be mandatory in biomass reforming. Extensive prior knowledge and experience with coal, oil, and natural gas can be used to modify, adapt, or design efficient catalysts. Most importantly, integration of catalyst, reactor, and process design and engineering in an early stage is needed.

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# **21** Biofuel-driven biorefineries for the co-production of transportation fuels and added-value products

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**Abstract:** This chapter discusses the importance of biorefining for optimal valorisation of biomass in a sustainable way. The focus is on conventional and advanced biofuel-driven biorefineries co-producing transportation fuels and added-value products from biomass. A definition for biorefining is presented. A classification system, the current status and future trends of biorefineries are discussed.

**Key words:** biorefining, definition, biorefineries, classification, biofuels, biofuel-driven biorefineries, biomass value chains.

### 21.1 Introduction

### 21.1.1 Biofuel production processes

The production of biofuels for transport, as alternative for the conventional crude oil derived transportation fuels gasoline and diesel, has gained a lot of interest in the last ten to 15 years, as a result of both the general approach to become less dependent on politically unstable countries and the concern about the consequences of anthropogenic CO<sub>2</sub> related global warming.

Both conventional biofuels (biofuels produced from crops that also could be used for food and feed production) and advanced biofuels (biofuels produced from non-food and non-feed crops) can be distinguished. Examples of advanced biofuels are: biochemically produced cellulosic ethanol, butanol and hydrogen, and thermochemically and catalytically produced Fischer-Tropsch diesel, methanol, dimethylether (DME), hydrogen, and synthetic natural gas (SNG). Also catalytically produced sugar derived furanics are examples of advanced biofuels for transport.

# 21.1.2 Giving value to the sustainable use of biomass – biorefineries

The production costs of advanced biofuels are too high to become market competitive without any governmental support. Technological breakthroughs are

necessary to change this situation. Currently, the main focus within the production processes is on the production of the specific biofuels concerned. Primary residues (residues resulting from crop farming) and secondary residues (process residues) are used for feed applications in case they meet the quality requirements, and to produce heat and/or power, both for internal process use and to be fed to the national grind. A major problem is that in case the biofuel production capacity increases the amount of residues will overload existing markets for these products, resulting in decreased market prices. This was illustrated by oil-crop biodiesel derived glycerine production in recent years, resulting in the closure of a lot of biodiesel production facilities in Europe. The same situation is now occurring for conventional bioethanol derived DDGS (dried distiller's grains with solubles). Another problem is that the production of heat and/or power from the process residues are low quality applications, resulting in relatively low market prices in case no governmental support is given (green power and/or heat support). The production of higher added-value Bio-based Products from these residues in integrated biorefinery facilities is necessary to maximise full biomass-to-products value chains, potentially making the production costs of the biofuels market competitive without any governmental support.

### 21.1.3 Biorefining: definition

International Energy Agency (IEA) Bioenergy Task 42 has developed the following definition for biorefinery (IEA Bioenergy, 2010):

Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals and/or materials) and bioenergy (biofuels, power and/or heat).

This means that biorefinery can be a concept, a facility, a process, a plant or even a cluster of facilities.

A main driver for the establishment of biorefineries is the sustainability aspect. All biorefineries should be assessed for the entire value chain on their environmental, economic and social sustainability. This assessment should also take into account the possible consequences due to the competition for food and biomass resources, the impact on water use and quality, changes in land-use, soil carbon stock balance and fertility, net balance of greenhouse gases, impact on biodiversity, potential toxicological risks and energy efficiency. Impacts on international and regional dynamics, end-users and consumer needs, and investment feasibility are also important aspects to take into consideration.

A biorefinery is the integral upstream, midstream and downstream processing of biomass into a range of products. A biorefinery can use all kinds of biomass, including wood and agricultural crops, organic residues (both plant and animal derived), forest residues and aquatic biomass (algae and sea weeds). A biorefinery should produce a spectrum of marketable products and energy. The products can be both intermediates and final products, and include food, feed, materials and chemicals; whereas energy includes fuels, power and/or heat.

The main focus of biorefinery systems which will come into operation within the next years is on the production of transportation biofuels. The selection of the most interesting biofuels is based on the possibility that they can be mixed with gasoline, diesel and natural gas, reflecting the main advantage of using the already existing infrastructure in the transportation sector. IEA Bioenergy Task 42 has defined that both multiple energetic and non-energetic outlets need to be produced to become a true biorefinery. The volume and prices of present and forecasted products should be market competitive.

Generally, both Energy-driven and Product-driven Biorefineries can be distinguished. In Energy-driven Biorefineries, the biomass is primarily used for the production of secondary energy carriers (biofuels, power and/or heat); process residues are sold as feed (current situation), or even better are upgraded to addedvalue bio-based products to optimise economics and environmental benefits of the full biomass supply chain. In Product-driven Biorefineries, the biomass is fractionised into a portfolio of bio-based products with maximal added-value and overall environmental benefits after which the process residues are used for power and/or heat production for both internal use and selling of the surplus to national grids.

A biorefinery is not a completely new concept. Many of the traditional biomass converting technologies such as the sugar, starch and pulp and paper industry used aspects connected with a biorefinery approach. However, several economic and environmental drivers such as global warming, energy conservation, security of supply and agricultural policies have also directed those industries to further improve their operations in a biorefinery manner. This should result in improved integration and optimisation aspects of all the biorefinery subsystems.

### 21.1.4 Biorefineries: classification

In literature, various types of biorefineries are dealt with (IEA Bioenergy, 2010), viz.:

- Green Biorefineries (GB), using 'nature-wet' biomass such as green grass, alfalfa, clover or immature cereals.
- Whole Crop Biorefineries (WCB), using raw materials such as cereals or maize.
- Lignocellulosic Feedstock Biorefineries (LCFB), using 'nature-dry' raw materials such as lignocellulose containing biomass and residues, including the more technology and/or main intermediate based concepts:
  - Thermo-chemical Biorefineries (TCB)/Syngas Platform (SG)
  - Bio Chemical Biorefineries (BCB)/Sugar Platform (SG)
  - Two Platform Concept Biorefineries (TPCB)
  - Forest Based Biorefineries (FBB)
- Marine Biorefineries (MB), using micro- or macro-algae (seaweeds), including:
  - Micro Algae Biorefineries (MAB)
  - Seaweeds (macro algae) Biorefineries (SB).

IEA Bioenergy Task 42 developed a more general classification system, better describing raw materials used, main intermediates (platforms) produced (a measure for the complexity of the biorefinery concept dealt with), and final products delivered.

The background for the proposed biorefinery classification system is the current main driver in biorefinery development, i.e. efficient and cost-effective production of transportation biofuels, to increase the biofuel share in transportation sector, whereas for the co-produced bio-based products additional economic and environmental benefits are gained. The classification system is based on a schematic representation of full biomass to end products value chains, distinguishing: raw materials, primary conversion processes, main biomass constituents (carbohydrates, lignin, proteins, fats, etc.), secondary conversion processes, platform intermediates, conversion processes and end products (see Fig. 21.1).

The platforms (e.g. C5/C6 sugars, syngas, biogas, bio-oil) are intermediates which are able to connect different biorefinery systems and their processes. The number of involved platforms is an indication of the system complexity of the biorefinery facility/concept. The two biorefinery product groups are energy (e.g. bioethanol, biodiesel, synthetic biofuels, power and heat) and products (e.g. chemicals, materials, food and feed). The two main feedstock groups are 'energy crops' from agriculture (e.g. starch crops, short rotation forestry) and 'biomass residues' from agriculture, forestry, trade and industry (e.g. straw, bark, wood chips from forest residues, used cooking oils, waste streams from biomass processing).

In the classification system, four main conversion processes are differentiated, including: biochemical (e.g. fermentation, enzymatic conversion), thermo-chemical (e.g. gasification, pyrolysis), chemical (e.g. acid hydrolysis, synthesis, esterification) and mechanical processes (e.g. fractionation, pressing, size reduction).

The biorefinery processes/concepts can be classified as:

A <specific platforms concerned> platform biorefinery for the production of <final products produced> from <name raw materials used>.

Some examples of classifications are:

- A C6 sugar platform biorefinery for the production of bioethanol and animal feed from starch crops.
- A syngas platform biorefinery for the production of FT-diesel and phenols from straw.
- A C6 and C5 sugars and syngas platform biorefinery for the production of bioethanol, FT-diesel and furfural from saw mill residues.

This classification system will be further extended and finalised in 2010 (IEA Bioenergy, 2010).





### 21.2 Biofuel-driven biorefineries: conventional biofuels

#### 21.2.1 Bioethanol

Current bioethanol production technologies are based on the conversion of carbohydrates derived from sugar cane, sugar beet, maize or cereals (i.e. wheat, barley) into ethanol. In addition, bioethanol can be derived from a number of other agricultural commodities such as cassava, or from residues or waste streams from other agro-industrial processes, including cane or beet molasses and starchy residues.

A number of by-products or co-products are produced during the conversion of biomass to ethanol. Most prominent by-product from ethanol production from corn, wheat or barley is so-called DDGS, which is a protein-rich fibrous residue that is primarily sold as animal feed. DDGS is formed by combining insoluble residues from the fermentation step with soluble residual streams from the distillation step, and drying the combined product. The market price of DDGS devaluated in the last 20 years due to increased production volumes saturating the feed market. Other high added-value products need to be found for DGGS to maintain its co-product status.

A common by-product of sugarcane derived ethanol is bagasse, which is the fibrous residue of the sugar cane stem after extraction of soluble sugars. Bagasse is commonly used to generate electric power and heat at the sugar mill facility to supply the energy needed for the bioconversion process.

Upgrading of process residues like DDGS and bagasse to higher added-value bio-based products (i.e. chemicals, materials) – turning the processes into biofueldriven biorefineries – maximises the sustainable valorisation of the raw biomass materials, increasing the market competitiveness of the bioethanol produced. DDGS is high in protein content (over 30%) which, if isolated, can be used potentially for the production of chemical precursors (Brehmer, 2008). Bagasse can also have many other applications such as the production of fibre boards or the production of high added-value specialty chemicals, i.e. xylitol from xylose-rich effluents from acid hydrolysis of sugarcane (Baudel, 2005).

Another by-product of bioethanol production is  $CO_2$ , which in certain cases is marketed as gas for industrial use.

#### 21.2.2 Biodiesel

Biodiesel is produced by reacting vegetable oils or animal fats with a low molecular weight mono alkyl alcohol (in most cases methanol). The so-called transesterification is typically performed at about 60°C in the presence of an alkaline catalyst such as sodium methoxide. For every ten tons of biodiesel produced about one ton of glycerol (or glycerine) is formed as a co-product.

In order to become more competitive and less dependable on politics, the biodiesel industry is looking for cheaper feedstocks, better control over feedstock

supplies, improved conversion technology and new ways to increase the value of glycerine.

A significant improvement in conversion technology may come from heterogeneous catalyst systems which give easier catalyst separation, enable higher conversions, and yield a higher quality crude glycerine than current homogeneous alkaline catalysts. Finding new outlets for glycerine is also vital for the biodiesel industry to become more competitive. A promising approach is to convert glycerol to fuel additives, commodity chemicals and polymer building blocks such as 1,2-propanediol; 1,3-propanediol or epichlorohydrin (Pagliaro and Rossi, 2008).

# 21.3 Biofuel-driven biorefineries: advanced biofuels

Most advanced biofuel production technologies today are focused towards converting lignocellulosic biomass into transportation fuels. Lignocellulosic biomass refers to plant biomass that is composed of cellulose and hemicellulose, which are natural polymers of carbohydrates and lignin. Cellulose and hemicellulose are tightly bound to the lignin by hydrogen and covalent bonds. Lignocellulose comes in many different types such as wood residues (e.g. sawmill residues), crop residues from agriculture (e.g. corn stover and cereal straws), industrial residues from agro-food processing operations (e.g. wheat bran and sugar beet pulp) and dedicated energy crops (primarily rapidly growing energy grasses such as *Miscanthus* and switchgrass, and wood species).

## 21.3.1 Biochemical routes - sugar platform

In order to distinguish biofuels derived from lignocellulose from those derived from existing agricultural commodities (see Section 21.2.1), often the term 'cellulosic' is added to the biofuel. This term indicates that these biofuels are based on converting the main carbohydrate fractions, cellulose and hemicellulose, of lignocellulosic biomass into fuels.

#### Cellulosic ethanol

Figure 21.2 shows a general schematic of the conversion of lignocellulosic biomass to bioethanol. The process consists of a pre-treatment step, a hydrolysis step and a fermentation step, followed by distillation and dehydration. In this process, lignin is discharged as a by-product and can be used to generate electricity to supply the process with energy or to export to the electricity grid.

Pre-treatment is necessary to break open the lignocellulosic structures and to facilitate the separation of the main carbohydrate fractions hemicellulose and cellulose from lignin, in order to make these better accessible for hydrolysis, the next step in the process (Mosier *et al.*, 2005). Pre-treatment is considered by



*21.2* Block scheme of production of lignocellulosic biomass conversion to ethanol.

many as the most costly step in lignocellulosic biomass conversion to ethanol. Pre-treatment may also significantly affect costs of subsequent steps in the process, including hydrolysis, fermentation as well as down-stream process steps (e.g. product separation). A variety of pre-treatment methods have been studied and some have been developed at pilot scale or demonstration scale. Current pre-treatment methods include: steam explosion, liquid hot water or dilute acid, lime, and ammonia pre-treatments (Maas, 2008). Pre-treatment methods using organic solvents such as ethanol or organic acids have been evaluated as well.

Hydrolysis is the process to convert the carbohydrate polymers cellulose and hemicellulose into fermentable sugars. Hydrolysis can be performed either chemically in a process involving the use of concentrated acids or enzymatically by using enzymes. Most pathways developed today are based on enzymatic hydrolysis by using cellulases and hemicellulases that are specifically developed for this purpose. Fermentation is the main process used to convert fermentable sugars, produced from the previous hydrolysis step, into ethanol. While in principal, the fermentation process is largely similar to that in the current ethanol production facilities, a major fraction of sugars produced from lignocellulosic are pentoses (5-carbon sugars such as xylose), which are difficult to ferment with standard industrial microorganisms. Therefore, a second important challenge in the conversion of lignocellulosic biomass to ethanol is the optimisation of ethanol-fermenting microorganisms that can convert all biomass-derived sugars, including xylose and arabinose. Furthermore, the efficient integration of various unit operations into one efficient facility is challenging. In some processes, the hydrolysis and fermentation steps are combined into one process which is often referred to as simultaneous saccharification and fermentation or SSF. Lignocellulosic biomass conversion to ethanol is currently in the pilot plant stage, with more than 30 pilot plants being operated or erected in both North America, the EU and elsewhere (IEA Task 39, 2009). Furthermore, in the recent years two demonstration plants for lignocellulosic biomass conversion to ethanol were erected in Canada and in Spain. In addition, one demonstration plant for cellulosic ethanol was commissioned in Denmark, and further plants are in the planning phases. All three demonstration plants were designed to use wheat straw as primary feedstock.

#### Cellulosic butanol

Butanol is of interest as a fuel for internal combustion engines. Butanol has a higher energy density and lower vapour pressure than ethanol, which makes it more attractive as fuel or blending agent. Butanol is produced during fermentation by solvent producing bacteria (e.g. Clostridia acetobutylicum) in a process that is generally referred to as ABE (i.e. acetone, butanol, ethanol fermentation). Production of butanol and acetone from biomass via fermentation started during World War I, but declined in the course of the twentieth century primarily due the lower production cost of non-renewable butanol produced by the petrochemical industry (Lopez-Contreras, 2003). However, with the increasing demand for renewable biofuels there is great renewed interest in fermentative production of butanol. Currently, a number of industrial facilities are producing butanol (Johnson, 2008), although uniquely from starch and sugar feedstocks such as corn and molasses. Production of ABE from lignocellulosic feedstocks (i.e. cellulosic butanol) is currently at the R&D stages. One of the main advantages of cellulosic butanol fermentation is that most solvent-producing bacteria can convert both pentose sugars (a main component of lignocellulose) as well as hexose sugars to butanol. Major challenges in further development of ABE processes at industrial scale are overcoming the low volumetric productivity of the fermentation, which requires development of new microorganisms for ABE fermentation that have a higher tolerance for the end products. In addition, a particular challenge in butanol fermentation is the efficient separation of the three end products acetone, butanol and ethanol (Ezeji et al., 2007). It is expected that with advances in cellulosic ethanol and, in particular, pre-treatment of lignocellulosic biomass, butanol production from lignocellulosic biomass will get further implemented.

#### Cellulosic hydrogen

Hydrogen is predicted to be an important energy carrier in the future. It can be produced from renewable biomass feedstocks either by thermo-chemical conversion or by biological conversion. The use of microorganisms for biological hydrogen production via fermentation is increasingly attracting attention recently (Hagen, 2006). Carbohydrates, such as sugars, starch or (hemi) cellulose, are the prime substrates for fermentative processes, including biohydrogen. For future sustainability of the energy supply, the utilisation of (hemi)cellulose is of prime interest, as this component is most abundant in crops that can be grown for the purpose of energy supply (de Vrije et al., 2009). In the proposed bioprocess, thermophilic and phototrophic bacteria are employed consecutively, producing clean hydrogen at small scale (Claassen and de Vrije, 2006). The utilisation of a great variety of biomass feedstocks has been studied within the last decade for biohydrogen production, in particular for thermophilic bacteria. Lignocellulosic biomass types that were evaluated for application to bio-hydrogen production include *Miscanthus*, delignified wood fibres (de Vrije et al., 2009), Sweet Sorghum Bagasse (Panagiotopoulos and Bakker, 2008) and barley straw and corn stalks (Panagiotopoulos et al., 2009). In general, thermophilic bacteria, including Caldicellulosiruptor saccharolyticus and Thermotoga Neapolitana, appeared to be able to simultaneously and completely utilise all soluble monomeric C5 and C6 sugars derived from pre-treated lignocellulosic biomass. In addition, these bacteria may also convert di- and oligosaccharides. Simultaneous and complete substrate utilisation from pre-treated lignocellulosic biomass will add to an energy-efficient process and would be a major advantage in industrial scale production facilities. As with cellulosic ethanol and butanol, advances in pre-treatment of lignocellulosic biomass achieved in the near future will greatly accelerate prospects for producing biohydrogen at the demo- or industrial scale.

#### Biofuel-driven biorefinery

The costs of lignocellulosic biomass derived advanced biofuels (i.e. ethanol, ABE and hydrogen) produced by biochemical conversion in general are too high to be market competitive without any governmental support. The production of added-value Bio-based Products from process residues like hemicellulose and lignin/stillage has the potential to significantly increase the market competitiveness of the total biomass-to-products value chain. Currently, a lot of effort is put in the development processes potentially being part of biofuel-driven biorefineries. Examples are technology developments for the conversion of hemicellulose to furfural-derived chemicals and pentoside surfactants; lignin/stillage to phenolics-derived wood adhesives, resins and thermosets; and cellulose to HMF and xylonic acids (Reith *et al.*, 2009).

## 21.3.2 Thermo-chemical routes - syngas platform

Much research, development and demonstration (RD&D) worldwide focuses on ways to produce advanced biofuels via thermo-chemical conversion of biomass feedstock. Making  $H_2$  and CO (syngas) from biomass is a crucial step in the production of most thermo-chemically derived advanced biofuels, for example Fischer-Tropsch (FT) diesel and methanol (Drift *et al.*, 2006). It is however not always necessary to convert all biomass into syngas; production of a gas containing  $H_2$  and CO, as well as several hydrocarbons (product gas), can also be sufficient (e.g. SNG).

As the approach towards advanced biofuels like FT-diesel and methanol is different from that towards SNG, both biomass value chains are discussed separately. This, however, does not mean that there are no synergies between them. In fact, combined production of both types of fuel can be an interesting alternative, in particular when SNG is one of the advanced fuels considered (Zwart and Boerrigter, 2005).

#### *Biomass-to-liquids (FT-diesel, methanol, DME, mixed alcohols)* from lignocellulosic biomass

For optimal synthesis of the advanced biofuels FT-diesel, methanol, dimethylether (DME), mixed alcohols and even pure  $H_2$ , a cleaned and conditioned bio-syngas is required. There are two major approaches in gasification to convert biomass into such a bio-syngas (Drift *et al.*, 2006): (1) Fluidised bed gasification with subsequent catalytic reforming, both at 900°C, and (2) Entrained flow gasification at approximately 1300°C with extensive pre-treatment. Both approaches require extensive syngas cleaning and conditioning, as shown in Fig. 21.3.

The fluidised bed gasification approach has the advantage that the gasification technology has been developed and already demonstrated with biomass for the production of heat and/or power. RD&D therefore mainly focuses on downstream catalytic reforming. The scale of implementation is, however, limited with the largest existing biomass gasification plants close to 100 MW<sub>tb</sub>.

Entrained flow gasification processes have already been developed and demonstrated on much large-scale for coal, e.g. the  $600 \text{ MW}_{\text{th}}$  Buggenum IGCC of NUON in The Netherlands. Biomass feedstock, however, needs to be pre-treated in



*21.3* Different pathways from biomass to biofuels with syngas as intermediate (Drift *et al.*, 2006).

order to take full advantage of the coal-based technologies. RD&D therefore focuses on pre-treatment such as flash pyrolysis for the production of a high energy density slurry and torrefaction for the production of a 'bio-coal', and on advanced process integration in order to increase efficiency and reduce overall costs. This last option includes the combination of black liquor gasification, biofuel production and chemical recovery in a pulp and paper mill (Landälv, 2006).

The scale of the gasifier is an important issue for most biomass-to-liquids plants. The fuel synthesis in general needs to be as large as possible because of the dominant economy-of-scale effect in biofuel synthesis and upgrading. However, a potential increase of the scale of the gasifier will result in higher feedstock costs due to higher transportation costs, even when considering pre-treatment and densification of the biomass before transportation (Zwart *et al.*, 2006a).

As raw bio-syngas resembles syngas produced from conventional fuels like coal and oil residues, the syngas cleaning will in most cases exist of relatively conventional systems based on filters, a Rectisol unit, and gas polishing by e.g. ZnO and active carbon filters. Also generally included will be a water gas shift reactor, providing the  $H_{2}/CO$  ratio desired for the different end-products.

#### Synthetic natural gas from lignocellulosic biomass

Biomass can be converted into a gas very similar to natural gas. This gas is called SNG or Substitute Natural Gas (bioSNG). It can be used as natural gas in any of its applications such as the production of power, heat and syngas, for example chemicals. Furthermore, SNG from lignocellulosic biomass can also be used as advanced biofuel. The availability of an existing natural gas infrastructure in countries like The Netherlands and the variety of potential applications are attractive arguments for the production of BioSNG.

The production of SNG from biomass starts with thermal gasification at temperatures of at least 800°C, where the biomass is converted into a combustible gas. Subsequent gas cleaning and upgrading results in two separate products, methane ( $CH_4$ ) and carbon dioxide ( $CO_2$ ). The methane is upgraded to the specification of the natural gas grid. The pure  $CO_2$  by-product can be wasted, but can also be sequestered in, e.g., underground geological formations to turn the whole biomass value chain into a net  $CO_2$ -extraction process beyond  $CO_2$ -neutral. The general process from biomass to SNG is shown in Fig. 21.4.



21.4 General process of biomass to SNG.

At the moment, there is no commercial plant producing bioSNG. Developments, however, have been started at the Paul Scherrer Institute (PSI) in Switzerland and the Energy Research Centre of The Netherlands (ECN) in The Netherlands, both have recognised that the gasifier's choice is crucial for the overall efficiency of the process (Meijden *et al.*, 2009; Rauch, 2009). Both have chosen the concept of indirect gasification to obtain an essentially N<sub>2</sub>-free gas with relatively high methane content. Additionally, indirect gasifiers do not need pure oxygen and therefore can do without an expensive and energy-consuming air separation unit. There are also some important differences which are summarised in Table 21.1. Included in the table is the process applied by DakotaGas in the US to produce SNG from lignite, in operation since 1984 (Stern, 2006).

As with almost all bioenergy processes, costs are mainly determined by the biomass costs, in particular at larger scales (Zwart *et al.*, 2009a, 2009b; Zwart *et al.*, 2006b). Therefore, SNG production costs are calculated for biomass prices of 0 and  $2 \notin /GJ_{th}$  (e.g. locally available biomass) as well as of 4 and  $6 \notin /GJ_{th}$  (e.g. biomass delivered at the gate of larger power plants). In Fig. 21.5, also reference is made to typical (commodity) prices for natural gas (grid as well as compressed), biogas, and biodiesel (the reference for the current European transportation fuel market), as valid on the Dutch market in 2007. With the natural gas commodity price as reference, it can be calculated that at sufficiently large scale, the cost of avoided CO<sub>2</sub>-emission can be below 60  $\notin$ /ton CO<sub>2</sub>, even at a reasonable biomass price of  $4 \notin /GJ$ .

	PSI	ECN	DakotaGas
Suitable for biomass?	Yes	Yes	No (unless mixed with coal)
Air separation (oxygen production)	No	No	Yes
Gasifier	Atmospheric indirect gasifier 'FICFB' (Ichernig <i>et al.</i> , 2008)	Atmospheric indirect gasifier 'MILENA' (Meijden <i>et al.</i> , 2008)	Pressurised fixed bed updraft Lurgi
Main gas cleaning	RME tar scrubber (Zwart, 2009)	OLGA tar removal (Zwart <i>et al.</i> , 2009)	Rectisol
Methanation	Fluidised bed process	Multiple fixed bed process	Multiple fixed bed process
Scale	10–50 MW	100+ MW	~3 GW
Main products	bioSNG and heat	$bioSNG$ and $CO_2$	SNG, CO <sub>2</sub> , tars
Energy efficiency solid fuel to SNG	~60%	~70%	~55%

Table 21.1 Main characteristics of SNG production processes



21.5 SNG production costs for different scales and biomass costs.

#### Biofuel-driven biorefinery

Both biomass-derived syngas (CO and  $H_2$ ) and SNG can be integrated into conventional existing petrochemical refinery complexes to produce both transportation fuels and chemicals from biomass. Also biochemically produced ethanol, butanol and hydrogen potentially can be used in the same existing refinery infrastructure to produce a variety of bio-based chemicals and materials.

An interesting technology for the production of the energy dense biomassderived intermediate bio-oil is fast pyrolysis (thermal degradation in the absence of oxygen). Currently, a lot of effort is being put into the (catalytic) hydrogenation of this material to make it suitable to produce biomass-derived fuel additives. Another development is the development of catalytic fast pyrolysis processes for the production of bio-based chemicals.

The synergistic combination of aquathermolysis (hot pressurised water treatment) and fast pyrolysis is a promising thermolysis option integrating fractionation of biomass with the production of valuable chemicals (de Wild *et al.*, 2009). Aquathermolysis causes hemicellulose to degrade and disappear from the raw materials. Lignin ether bonds are broken, but the lignin is hardly affected. Cellulose is also retained and seems to become more crystalline (see Fig. 21.6).

#### 21.3.3 Combined bio- and thermo-chemical routes

Currently, secondary (process) residues of biochemical conversion processes, for example lignin, are used in thermo-chemical conversion processes (combustion)



21.6 Aquathermolysis-pyrolysis biorefinery concept.

to produce heat and/or power, partly used to energetically drive the biochemical conversion process. However, specifically for lignin a variety of downstream valorisation processes are being developed to produce more financial value out of this secondary residue stream, for example supercritical lignin conversion, enzymatic lignin conversion and catalytically supported fast pyrolysis (see Fig. 21.7).



21.7 Lignin valorisation process (de Wild (IEA), 2010).

## 21.4 Optimising biomass value chains

Different types of biomass, whether these are primary crops or residues, are applied nowadays as the raw material for biofuels. These raw materials are used just for their caloric value. Both direct (oil) and indirect use, after conversion of the biomass into a liquid component, preferably with an increased caloric value per volume, are distinguished. Ethanol or butanol are good examples of the latter.

Other components that are present in the biomass crops or their residues are often regarded as primary residues, however, these components could have significant value, and their valorisation could well contribute to the economic feasibility of the overall biofuels production process as well (Brehmer *et al.*, 2009).

Thermal processing of biomass has the advantage that the heterogeneous biomass components are converted towards a much more homogeneous mixture, i.e. syngas or pyrolysis oil (Manurung *et al.*, 2009). These processes, however, will not benefit from the presence of the specific components that are not easily converted into biofuels but could create value because of their functionality on a molecular level or on a macroscopic level, e.g. as construction material or as a product to make paper.

Functionalised bulk chemicals offer great economic potential, if one wants to substitute fossil raw materials by biomass, since these chemicals need to be synthesised using, apart from oil, large quantities of energy. The production of these chemicals conventionally also requires high capital costs due to the fact that many conversion steps are necessary to convert raw oil via naphtha and ethylene to these more complex functionalised chemicals (Sanders *et al.*, 2007).

In plant material often molecular functionality is present that can be used to make the same bulk chemicals as nowadays by petrochemical processes, but now with short synthesis routes starting from biomass (Haveren, 2007; Scott, 2007). Certainly not all components in biomass represent these high values; also biofuels, power, heat and soil improvers like fertilisers will contribute to the overall valorisation of raw biomass materials.

When more than one product is produced from a biorefinery unit, the logistics and pre-treatment become more important (Bennett, 2009). Because the transport of water and minerals is not very sustainable, the first pre-treatment and fractionation steps will be performed close to the biomass production fields. This favours small scale operations close to the fields that make intermediate products that are easy to transport and that do not deteriorate in time. Questions that still have to be solved are: (1) how can small scale processes that do not suffer from diseconomy-of-scale, and preferably can operate more economically on small scale than on large scale, be developed? and (2) how sustainable are these processes taking into account People, Planet and Profit issues?

#### 21.4.1 Choice of raw materials

Once one is able to valorise residue streams, there will be a challenge to look for even better raw materials that contain a higher proportion of the previously called residue stream. Finally, one can try to optimise the culture on the field or even the genetic optimisation of the crop that contains more of that previously called residue component, and at the same time improve the crops processability by genetic means.

Good examples of genetic modification of primary crops have been obtained for the amino acid lysine in crops like potato (Voorst, 1999) and corn (Houmard, 2007). These improvements were initiated because of the application as animal feed ingredient. Recently, itaconic acid has been expressed in potato with the aim to use this as building block for the synthesis of methacrylate.

Primary residue streams such as wheat straw and other agricultural residues can be used for their cellulose content, but sometimes they still consist of other valuable components such as proteins as is the case for sugar beet or sugar cane leaves (trash), for the leaves of cassave, and other crops. Until now these plant components almost never had an economic application, but now have potentially become an interesting alternative for the fossil based resources.

DDGS and rapeseed meal are good examples of so-called secondary residue streams, i.e. residues that result from industrial processes (often in the food industry), and recently result from the biofuels industry. These fractions have similar compositions as primary residues with the logistic advantage that these streams are available from one point source. These streams therefore often have already some applications as e.g. compound feed components. It is not only that separation of components gives a higher value to each single component but also the removal of a component such as phosphate or potassium, that in too high concentrations have a negative value in actual compound feed applications, can help to increase the economic feasibility of biorefining primary and secondary residue streams.

# 21.4.2 Economy-of-scale versus economy-of-duplication and the choice of unit operations

Economy-of-scale contributes to profitability because less investment is required per unit product manufactured. This economy-of-scale is often explained because the volume of a reactor increases with the power of three while the investment itself increases often with the power of two since this is dependent on the outer surface of the reactor itself (Lange, 2001). When major heat exchange capacities are required, the need for larger factories becomes apparent because the surface of heat exchangers needs to be in correlation with the volume of the reactor or in other words with the amount of heat that is produced in the volume of the reactor. If one could circumvent the need for heat exchangers, then the need for building large units will diminish and many small units can do the job that initially was done by the large factory. This will enable a totally different architecture of the processes and certainly of the logistics of biomass value chains.

Raw materials that contain a lot of water, and that are perishable, and before were not attractive to be transported to a large factory, can nowadays be (pre) processed at small scale. Cassave roots are a good example of this (Sanders *et al.*, 2005). Ten small scale mobile factories of 4000 tons of starch product each are in operation at different locations in Nigeria. Also residues like beet leaf or carrot leaf can now be pre-processed, as is the case for meadow grass. It will be understood that for other crops that contain a lot of water like potato and grass, small scale processing will have a lot of advantages. Developments of small scale production of ethanol from corn is in progress in The Netherlands, where because of the reduction of unit operations that need heat exchange, the capital cost per litre of ethanol is not higher for these small units than for the large scale corn to ethanol plants in the USA, that operate at 100 times larger scale (Sanders *et al.*, 2008).

## 21.4.3 People, planet, profit

In case we can use more than just the component that is suitable as biofuel, and not waste all other components, we reduce the amount of biomass. We also reduce the land surface we require to substitute fossil resources, the amount of water and the amount of minerals which would be required if all of the applications would be produced from individual biomass resources. By closing loops in short circles, as is the case for water and minerals that are separated from the biomass fractions in small processing units, we prevent the loss of these valuable fertilisers. By small scale pre-processing we reduce the need for transportation.

More crop residues that now are wasted can be valorised. Small scale processing means that less capital investment is required to start a business. More people can start up their business but certainly more work can be done by farmers themselves. People will be less dependent on large companies and can work for their own future, invest in equipment and education of their children.

Small scale operations will eventually become available for poor developing countries because the absolute amount of money that is required is modest even under African conditions (Goense, 2006).

Since more raw materials will be available to be processed, and more people can afford to build a factory, the total volume of fossil resources that can be substituted under economic conditions will grow rapidly.

# 21.5 Current status and future trends

Currently, the main focus in both conventional and advanced biofuel production processes is on the production of the specific biofuels rather than on the development of processes that maximise the valorisation of the raw materials to both bioenergy and bio-based products in a sustainable way. Valorisation of both primary and secondary biofuel chain and process residues to added-value bio-based products (chemicals, materials) is the short term option for upgrading of these processes to integrated biorefinery processes, maximising the overall valorisation of the raw materials concerned, minimising the biofuel production costs, and thereby increasing their market competitiveness.

Integration of both biochemical and thermo-chemical biomass conversion processes into already existing petrochemical infrastructures is another short term option to valorise biomass to both bio-based products and biofuels, greening their fossil counterparts.

Development of relatively small-scale concepts seems to be a favoured option to introduce more advanced (green and whole crop) biorefinery processes into the market at mid-term. These concepts require less initial investment which is an advantage for the industrial stakeholder support for the introduction of new risky initiatives and because of the economy-of-duplication these concepts are expected to become market competitive soon. These concepts will create the perceptional, socio-economic and environmental framework for the introduction of even more advanced (lignocellulosic feedstock and marine) biorefinery concepts at larger scale on the longer-term.

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**Abstract:** The valorization of by-products helps to reduce waste, to minimize the footprint of the technology and to add value through the production of biodiesel as an energy carrier. Alternative resources such as deodorizer distillates can partially replace the traditional feedstocks for the production of biodiesel, but require application of new technologies and/or additional purification steps. This chapter proposes to offer an overview of different methodologies used to convert deodorized distillates to biodiesel/biofuels and to recover the valuable minor components such as sterols, squalene and tocopherols.

**Key words:** biodiesel production from deodorizer distillates, conversion routes for high-acidity feedstocks, recovery of the minor components.

## 22.1 Composition of deodorizer distillate

Crude vegetable oils contain triacylglycerols (TAG) as major component and various minor components such as diacylglycerols (DAG), monoacylglycerols (MAG), free fatty acids (FFA), phospholipids, tocopherols, sterols, squalene, color pigments, waxes, aldehydes, ketones, triterpene alcohols and metals which may affect the quality of the final product. These minor components are removed partially or entirely by either physical (RBD) or chemical (NBD) refining.

Deodorizer distillate (DD) is one of the side streams obtained in the final step of refining of vegetable oils used to remove odoriferous components and to reduce the free acidity in order to make the vegetable oils suitable for human consumption.

It was observed that the composition of DD is dependent on the oil source, the refining routes (physical or chemical) and the deodorizer operating conditions (De Greyt and Kellens, 2000; Kellens and De Greyt, 2000). Determination of the DD composition or stability was studied by different authors (Haas and Scott, 1996; Verleyen *et al.*, 2001; Dumont and Narine, 2007; Dumont and Narine, 2008). DD obtained from physical (RBD) and chemical (NBD) refining of different feedstocks contains typically 30–90% FFA, an important unsaponifiable matter such as tocopherols, sterols and squalene (5–33%), but also acylglycerols (<1–14%) (Table 22.1).

Physical (RBD) and chemical (NBD) refining differ both in the composition of the deodorized oil and of the distillate.

It was observed that physically refined oils have a higher retention of unsaponifiables in the oil compared with the chemically refined oils. A sterol retention varying

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Compounds	Deodorizer distillates (%)		
	RBD*	NBD**	
Water	_	_	
Free fatty acids	80–90	30-60	
Acylglycerols	<1–14	5–12	
Phospholipids	-	-	
Unsaponifiable matter	5–10	25–33	

#### Table 22.1 General composition of DD

Source: Echim et al. (2009).

\* RBD = physical refining (refined, bleached and deodorized) \*\* NBD = chemical refining (neutralized, bleached and deodorized)

between 68% and 90% in the physical and 79% and 87% in chemical refining is observed while tocopherol retention between 23% and 92% in the physical and 21% and 73% in chemical refining was found. The higher retention of unsaponifiables in the physically refined oil is attributed to the lower vapor pressure of these components due to the advance of FFA during deodorization (Verleyen *et al.*, 2002).

DDs obtained from the chemical refining are rich in tocopherols and sterols and contain little FFA. On the contrary, distillates derived from physical refining contain mainly FFA and consequently little tocopherols and sterols representing little economic value.

Deodorization has an important effect on the overall refined oil quality and distillate composition. The last decade's increased attention has therefore been paid to the optimization of the deodorizing process conditions and the development of improved deodorizing technology (Verleyen *et al.*, 2002).

The development of a new type of scrubber operating at two different temperatures (dual condensation concept) allows the production of DDs with a unique composition (high in tocopherols and sterols) and higher value (Kellens *et al.*, 2005).

A modification to the condenser unit was made for the collection of the distillate in two separate fractions. The first fraction contains mainly FFA (80%) where the second fraction contains concentrated sterols and tocopherols (17% and 15%, respectively) and residual FFA (43%) with a similar composition as DD from chemical refining (Verleyen *et al.*, 2002).

### 22.2 Applications and estimates of deodorizer distillates

DD represents a good source of valuable minor compounds such as sterols, tocopherols and squalene, which can be recovered and further used as food

additives, in the pharmaceutical industry and cosmetics. Furthermore, the FFAs, one of the major compounds present in DD, are mostly used as additives for animal food, fluidizing agents, for lecithin or as medium-grade soaps. Such fatty acids can also be used as precursors in a wide variety of molecular synthesis schemes such as the production of dibasic acids of different chain lengths (Gangopadhyay *et al.*, 2007). Alternatively, DD has non-food applications, such as their mixing with fuel oil (5–10%) to fire steam boilers (Svensson, 1976). A great interest was shown in DD for its possible application in the production of high-quality (biodiesel) or low-quality (biofuel) methyl esters.

Rough estimates of the quantity of DD are available. The amount mainly depends on the content of FFA, gums and impurities present in the oil and on the efficiency of refining. Using Mielke (2009) figures for the worldwide vegetable oils production in 2009 and assuming that (1) palm oil is entirely physically refined (100% RBD), (2) soybean oil is mainly chemically refined (100% NBD) and (3) rapeseed and sunflower oils are mainly physically refined (75% RBD/25% NBD), one can estimate the DD production. Considering that by physical refining a multiple of 1.2 times the FFA content is removed from crude oil as DD (Vries, 1984), the DD production can be estimated (Table 22.2). The FFA content before deodorization step for the chemically refined oil (NBD) is difficult to estimate. However, it is generally considered that the vegetable oil contains ca. 0.10% FFA before deodorization and 0.05% FFA after deodorization (final oil) in order to make it suitable for human consumption.

The palm oil production increased significantly in 2009 (46.5 mil.t/year) compared with 2007 (36.8 mil.t/year) that accordingly determined an increase in the DD (RBD).

Considering Mielke (2009) figures for the vegetable oil production in 2009, approximately 3.1 mil.t/year of DD should have been produced, where 3.02 mil.t/ year comes from physical refining (DD-RBD) and 0.03 mil.t/year comes from chemical refining (DD-NBD).

Oil crop	Oil production <sup>#</sup> (mil.t/year)	FFA (%) in the crude oils	DD (RBD)‡ (mil.t/year)	DD (NBD)† (mil.t/year)
Palm	46.50	4.00–5.00	2.23–2.79	_
Soybean	37.50	0.10*	-	0.022
Rapeseed	22.40	0.10*-1.00	0.20	0.003
Sunflower	12.00	0.10*-3.00	0.32	0.002

Table 22.2	Estimates	of deodorizer	distillate	production
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\* %FFA before deodorization.

 $\dagger \text{ DD (NBD)} = 1.2 \times 0.05 \text{ \%FFA}.$ 

 $\pm$  DD (RBD) = 1.2 × % FFA of crude oil (Vries, 1984).

# Mielke (2009).

Owing to the high content of FFA present in the DD from physical refining (RBD), this side-product is suitable for the biodiesel production and the DD from chemical refining (NBD) is mainly valorized for the recuperation of minor compounds. However, there is no clear distinction in the literature of the origin of the feedstocks.

# 22.3 Production of biodiesel/biofuel from deodorizer distillates

This chapter proposes to offer an overview of different processes used to convert DD to biodiesel/biofuel. Additionally, different processes to recover valuable minor components are described where conversion of FFA and/or acylglycerols to FAME (fatty acid methyl ester) was applied in order to facilitate their purification. However, most of the literature study targets either quality of biodiesel/biofuel or quality of the minor components and seldom offer aspects regarding the overall quality of obtained by-products.

# 22.3.1 Introduction

An overview of the described routes for biodiesel/biofuel production was given by Echim *et al.* (2009). Biodiesel/biofuel can be produced from DD by direct esterification (Fig. 22.1) of the FFA or by conversion of FFA to acylglycerols prior to transesterification (Fig. 22.2).

# 22.3.2 Production of biodiesel/biofuel by direct conversion

#### Chemically catalyzed process

Soragna (2009, personal communication) described the industrial process for the conversion of FFA into FAME using heterogeneous catalyst, called FACT (Fatty Acid Conversion Technology). This technology is an alternative option compared to the classical technology using homogeneous catalyst, consisting of a continuous countercurrent multiple step esterification using solid catalyst in fixed bed reactors, at 90°C and 0.35 MPa. Production of biodiesel/biofuel from feedstocks with high acidity by direct conversion was registered as a 'stand-alone process' Fig. 22.3(a).

For feedstocks with medium/high acidity an 'integrated process' was applied (Fig. 22.3b) where a transesterification step for the conversion of the acylglycerols was also included. The FFAs were distilled off and further esterified to FAME before the transesterification of the residual acylglycerols.

The advantage of these processes is the possibility to process high diversity acidity feedstocks (up to 100%) with a conversion of up to 99.8% without limitation in capacity, no usage of liquid acids, higher quality by-products and mild operating conditions.



*22.1* Production of biodiesel/biofuel by direct conversion route (from Echim *et al.*, 2009).

Verhé *et al.* (2008) reported a process of converting the DD to biodiesel using sulfuric acid as catalyst, at 75°C for 5 h. The FFA and MAG have undergone esterification, resulting in methyl esters. The crude biodiesel was further washed, dried and distilled in order to increase the quality of the methyl esters. The distillation pitch was further processed for the recovery of sterols and tocopherols.

An extensive study was carried out by Chongkhong *et al.* (2007) on the palm fatty acid distillate (PFAD) (93% FFA), as feedstock for a batch and continuous production of biodiesel. For the continuous process (CSTR), the amount of FFA was reduced from 93% to less than 2% at the end of the esterification process. A further treatment consisting of neutralization of the FFA and transesterification of the glycerides was required in order to obtain biodiesel which complies with the specifications.

Facioli and Barrera-Arellano (2002) described a process to obtain ethyl esters from soybean oil deodorizer distillates (SODD) using concentrated  $H_2SO_4$  as catalyst. The DD contained 47% FFA, 26% acylglycerols and 26% unsaponifiable matter.



*22.2* Production of biodiesel/biofuel via acylglycerols route (from Echim *et al.*, 2009).

A conversion of 94% of the fatty acids to ethyl esters was achieved. However, the acylglycerols were not affected and the losses of tocopherols were around 5.5%. A molar excess of ethanol in relation to SODD:FFA was found to be necessary to obtain the best conversion.

Hammond and Tong (2005) described a three-stage acid catalyzed esterification. The reaction mixture was centrifuged, the supernatant lipid phase was separated from the sludge (glycerol, water, acid and methanol), and further reacted with methanol and acid. The maximum FAME conversion obtained for 12-tested acid oils averaged 81%. However, the ester phase could not be increased above 85% even after a fourth-stage reaction or if a basic catalyst was used in large excess. Unknown materials were reported in both FAME and in the sludge phase having a hydrophobic and hydrophilic behavior, respectively. The former compound caused an increase of the biodiesel viscosity and is hypothetically attributed to the presence of polymers.



22.3 Fatty Acids Conversion Technology (FACT) to produce biodiesel/ biofuel from low-quality raw materials: (a) stand-alone process(b) integrated process (from Soragna, 2009, personal communication). The polymers might have been formed during the soap acidulation process or during the esterification reaction, due to the limited supply of methanol and the long reaction time. The compound could not be further removed by distillation.

#### Enzymatically catalyzed process

The lipase-catalyzed methyl esterification of the fatty acids present in canola oil deodorizer distillates (CODD) was studied by Ramamurthi *et al.* (1991).

CODD was esterified to methyl esters, using immobilized lipase *Randozyme SP-382* as catalyst. Conversion of the FFA up to 96% was achieved without the use of vacuum or a dehydrating agent.

It was found that three variables, namely moisture content of the enzyme, reaction time and the amount of molecular sieves, did not exhibit any profound effect on the conversion rate. On the contrary, the ratio of the reactants had a significant effect on the conversion equilibrium and showed a high interaction effect along with the temperature. High conversion (>90%) was obtained at combinations of both high temperature (70°C) and low ratio of reactants (1.2) and for combinations of low temperature (50°C) and high ratio of reactants (2.0). It was observed that higher concentrations of enzymes could compensate the negative effect of increased temperature. The conversion of acylglycerols was not investigated in this study, since the esterification was considered as a preliminary step for the recovery of tocopherols and sterols.

Facioli and Barrera-Arellano (2001) investigated the enzymatic esterification of the FFA from SODD with ethanol using immobilized fungal lipase (Lipozyme<sup>IM</sup>) as biocatalyst. SODD contained 47% FFA, 26% neutral oil and 26% unsaponifiable matter. The best conversion was above 88% with no tocopherol losses.

The esterification of SODD with butanol, using *Mucor miehei* lipase as biocatalyst and SC-CO<sub>2</sub>, has been described by Nagesha *et al.* (2004). The feedstock was preliminary filtered in order to remove sediments and sterols and enzymatic hydrolyzed to FFA using immobilized lipase (*Candida rugosa*) in SC-CO<sub>2</sub> reactor unit. Hydrolyzed SODD containing <88% FFA was further enzymatically esterified with *M. miehei* in presence of butanol, with a maximum yield of 95% FABE. The content of acylglycerols was not affected by esterification. The high content of residual glycerides (3%) present in the final FABE impeded its direct use as biodiesel.

Wang *et al.* (2006) described a process for simultaneous conversion of FFA (28%) and acylglycerols (60%) from SODD to alkyl esters using a mixture of two enzymes (3% Lipozyme TL IM and 2% Novozym 435) in the presence of *tert*-butanol as co-solvent. It was found that the negative effects on the enzyme stability caused by the excessive methanol ratio and by-product glycerol could be completely eliminated by using *tert*-butanol. The lipase activity remained stable after 120 cycles. The maximum yield of FAME (84%) was achieved with an

increase of *tert*-butanol content up to 80% (based on the oil weight). However, a further increase of the solvent resulted in a decrease of the methyl esterification (ME) yield which was explained by the dilution effect on reactants.

Fine-porous silica gel and molecular sieves (3Å) were found to be effective to improve biodiesel yield by controlling the water concentration formed as a by-product during the reaction. A conversion yield of 97% could be achieved when the 3Å molecular sieves quantity was 10 times the maximal water weight (calculated from FFA) and 93% with less than 10 times silica gel as adsorbent. However, more than 10 times silica gel led to a decrease in the ME yield, which was explained by the reduced availability of methanol for the methanolysis due to its absorbance by silica.

Du *et al.* (2007) investigated the enzymatic esterification of SODD containing 28% FFA, 60% TAG and 6% tocopherols. The reaction was a lipase-mediated methanolysis using Novozym 435 as catalyst, at 40°C in a solvent-free medium. The enzyme kept its activity after being reused for 10 cycles, each cycle being 24h. The highest biodiesel yield of 95% was achieved by adding tenfold molecular sieves (3Å). The investigation of the lipase to methanol tolerance revealed that the lipase could maintain its stability and activity in the presence of methanol at even a three molar concentration. This tolerance was attributed to the presence of other compounds than TAG, namely FFA, sterols and tocopherols. A linear relationship between the FFA content and the lipase tolerance to methanol was observed but the presence of sterols and tocopherols showed no effect.

#### 22.3.3 Production of biodiesel/biofuel via acylglycerol route

Another approach reported in the literature for the conversion of DD consists in esterification of FFA with glycerol to form acylglycerols as an intermediate step in the production of biodiesel/biofuels.

Synthesis of MAG from DD was mainly studied due to the large number of applications as additives, for enhancing plasticity of fats or as bases in the food, medicine and cosmetic industry. Among synthesized acylglycerols, the monoester has the highest surface activity, and therefore, its concentration is very important for direct usage of the reaction product as an emulsifier.

The esterification of glycerol with fatty acids leads normally to a mixture of MAG, DAG, and TAG and some amount of unreacted substrates. The proportions depend on the presence and type of catalyst, as well as the reaction conditions such as temperature and the molar ratio FFA:glycerol.

Studies showed that enzymes have an enormous potential as catalysts in the processes where high regioselectivity is required (Lo *et al.*, 2005). However, for the large-scale synthesis, the processes are not yet competitive due to the high cost of the enzyme.

Different studies summarized hereafter describe processes for the synthesis of acylglycerols in order to decrease the acidity of the feedstocks. These processes

are catalyzed either enzymatically or conducted under non-catalytic conditions. However, the step of transesterification of acylglycerols to FAME was not further described in order to evaluate the final quality of the biodiesel.

#### Enzymatically catalyzed process

Lo *et al.* (2005) reported a process to synthesize acylglycerols (mainly DAG) by lipase-catalyzed esterification of glycerol with fatty acids from corn oil deodorizer distillate (CoDD). It was found that Lipozyme RM IM was the most effective among the commercial 1,3–position-specific screened lipases. A DAG yield of 70% was obtained.

Tangkam *et al.* (2008) described the enzymatic esterification in a solvent-free medium of different DD resulting from the refining of various vegetable oils. A direct esterification of mixed distillates (61% FFA and 39% acylglycerols) with glycerol using immobilized lipase B from *Candida antarctica* (Novozym 435) led to moderate proportions (46%) of DAG. Application of a two-stage reaction consisting of a hydrolysis step of DD to increase the FFA content followed by esterification with glycerol led to a higher formation (>61%) of DAG. Furthermore, it was observed that the high initial concentration of unesterified fatty acids in the distillate (100% FFA) has a positive influence on the concentration of DAG in the final product (>71%). Enrichment of DAG in the final products by short-path vacuum distillation led to concentrates containing up to 94% DAG, ca. 5% TAG and no unesterified fatty acids and MAG. Increase in temperature strongly affected the rate of esterification, whereas the influence of the reaction pressure was only moderate.

#### Non-catalytic process

Smet (2008) described a process for the esterification of fatty acid distillate (93% FFA) with technical grade glycerol. The novelty of the process consists in synthesizing acylglycerols in a relatively short time (<6 h) without the use of catalysts obtaining a final yield of 86%.

However, the FFA content was still high, a distillation step of the residual FFAs and glycerol was necessary in order to increase the purity of the synthesized acylglycerols. The by-products of distillation were further reused as reaction products in the synthesis of acylglycerols.

# 22.4 Recovery of sterols, tocopherols and squalene from deodorizer distillate

#### 22.4.1 Introduction

For the recovery of minor components a lot of research has been reported. However, industrial applications of the described processes are not much published, except for in the patent literature. In the production of biodiesel/biofuel from DD, its heterogeneous composition (FFA, acylglycerols, sterols, squalene and tocopherols) should be considered, not only for the selection of a good conversion process but also for the valorization of all the compounds which would make the process economically more interesting.

For their purification, different aspects should be considered. Since bioactive compounds, such as tocopherols, phytosterols and squalene, are minor components in DD, their enrichment is vital before they can be effectively fractionated and separated into an individual compound. The main challenge is to separate them from each other, especially in the case of the following pairs of components: tocopherol–squalene, tocopherol–fatty acids, tocopherol–sterol and sterol–squalene.

Numerous methods have been proposed for treating DD to isolate one or more compounds. In general, the selective separation of compounds in DD is based on differences in their chemical and physical properties such as solubility, polarity, molecular weight or differences in volatility.

Molecular distillation or short-path distillation is by far the preferred method for isolating both thermosensitive and high molecular weight compounds (Top *et al.*, 1993; Shimada *et al.*, 2000; Watanabe *et al.*, 2004; Martins *et al.*, 2005; Nagao *et al.*, 2005). However, the disadvantages of this method are that the equipment is expensive and the operation cost is high. Furthermore, the sterols are one of the major components of DD and cannot be removed by molecular distillation because their molecular weights and vapor pressure are similar to those of tocopherols. A conventional method to concentrate tocopherols using molecular and vacuum distillation after removing the sterols via alcohol recrystalization requires several steps such as solvent recovery and purification, and further requires high amounts of solvents and energy.

Other separation processes are based on differences in their polarity like solvent extraction (Brown and Smith, 1964; Chu *et al.*, 2002; Gunawan *et al.*, 2008; Leng *et al.*, 2008). The advantage of solvent extraction over molecular distillation is that it operates under atmospheric pressure and lower temperature, and requires simpler equipment. Although modified solvent extraction is capable of separating tocopherols, free phytosterols, FFA and acylglycerols from DD on laboratory scale, it is difficult to apply this method in large-scale operations.

Other processes involve supercritical fluid extraction (Lee *et al.*, 1991; Bondioli *et al.*, 1993; Stoldt and Brunner, 1998; Stoldt and Brunner, 1999; Chia-Cheng *et al.*, 2000; King and Dunford, 2002; Mendes *et al.*, 2002; Mojca *et al.*, 2003; Nagesha *et al.*, 2003; Pereira *et al.*, 2004; Liu *et al.*, 2006; Vázquez *et al.*, 2006; Fang *et al.*, 2007; Vázquez *et al.*, 2007; Fornari *et al.*, 2009; Torres *et al.*, 2009; Martinez-Correa *et al.*, 2010), crystallization (De Areal Rothes and Verhé, 2005; Pan *et al.*, 2005), crystallization and/or membrane separation (Lin *et al.*, 2007), treatment with urea (Sampathkumar, 1986; Maza, 1992) and batch adsorption (Chu *et al.*, 2004; Fabian *et al.*, 2009).

Solvent extraction and crystallization are mainly used to recover sterols over tocopherols. This process has the advantage of not causing tocopherol oxidation



22.4 Schematic representation of the routes used to separate the minor components.

and does not use high pressure, but the amount of solvent required is still very high and the use of such quantities does not lead to an environmentally friendly process. It is also noted that extraction with solvent requires laborious manipulations. Research in this area is not very extensive due to the low recovery and low purity of sterols and tocopherols (Lin and Koseoglu, 2003; Moreira and Baltanas, 2004).

Besides the target compounds (sterols, tocopherols and squalene), the DD contains acylglycerols and FFA which make the purification more difficult. Consequently, it is necessary to modify DD with esterification and/or alcoholysis reactions using chemical or enzymatic means, which convert most of the fatty acids, free sterols and acylglycerols to FAME and esterified sterols.

A schematic representation of the most used pathway to separate the minor components is shown in Fig. 22.4.

## 22.4.2 Separation of minor components by distillation

Shimada et al. (2000) converted free sterols in SODD to sterol esters and completely hydrolyzed acylglycerols by applying an enzymatic reaction to the

purification of tocopherols and sterols. Fractionation of these two compounds of interest was carried out by short-path distillation. It was found that C. rugosa lipase recognized sterols as substrates but not tocopherols, and that esterification of sterols with FFA could be effected with negligible influence on the water content. High boiling point substances, including steryl esters, were removed from the SODD by distillation, and the resulting distillate (SODDTC) was used as a starting material for tocopherol purification. Several factors affecting esterification of sterols were investigated. It was observed that approximately 80% of sterols were esterified when tocopherols were unmodified. After the reaction, tocopherols and FFA were recovered as a distillate by molecular distillation of the oil layer. To enhance further removal of the remaining sterols, the lipase-catalyzed reaction was repeated on the distillate. As a result, more than 95% of the sterols were esterified in total. The resulting reaction mixture was fractionated to four distillates and one residue. The main distillate fraction contained 65% tocopherols with low contents of FFA and sterols, and the residue fraction contained high-purity steryl esters. It was suggested that due to the fact that the process presented in this study included only an organic solvent-free enzymatic reaction and a molecular distillation, it could be feasible as an industrial purification method for tocopherols. However, the process had the drawback that FFA and tocopherols were not efficiently fractionated since the boiling points of the two compounds were close.

Watanabe *et al.* (2004) introduced the chemical modification of the DD to convert FFA to their methyl or ethyl esters, followed by short-path distillation of the reaction mixture for the elimination of fatty acid esters and thus the purification of tocopherols and sterols esters.

Tocopherols and sterols in the SODD were first recovered by short-path distillation, which was named SODD tocopherol/sterol concentrate (SODDTSC). The SODDTSC which contained MAG, DAG, FFA and unidentified hydrocarbons in addition to the two compounds of interest was then treated with a lipase to convert the free sterols to fatty acid steryl esters (FASEs), acylglycerols to FFA and FFA to FAME. It was observed that methanol inhibited the esterification of the sterols. Hence, a two-step in situ reaction was conducted and a conversion of 80% of the initial sterols to FASEs, complete hydrolysis of the acylglycerols and a 78% decrease in the initial FFA content by methyl esterification, was achieved. To enhance the degree of steryl and methyl esterification, the reaction products (FASEs and FAME) were removed by short-path distillation, and the resulting fraction containing tocopherol, sterols and FFA was again treated with the lipase. Distillation of the reaction mixture purified the tocopherols to 76% (recovery, 89%) and sterols to 97% as FASEs (recovery, 86%).

Nagao *et al.* (2005) described a process where SODD was first distilled and the sterols and tocopherols were enriched. The obtained fraction was SODDTSC. In this study, esterification of sterols was improved by removing water with a degree of esterification of 95%. The second-step reaction was then conducted in which

95% FFAs were converted into FAME. Finally, tocopherols and steryl esters were purified from the reaction mixture by short-path distillation. Tocopherols were purified to 72% (88% yield) and steryl esters were purified to 97% (97% yield).

Purification on a larger scale was performed with 1.5 kg SODDTSC and the procedure is shown in Fig. 22.5.

Albiez *et al.* (2004) described a process for concentrating and isolating sterols and/or tocopherols from physically refined DD that consisted in hydrolysis to split the glycerides present into FFA and glycerol, followed by the glycerolcontaining hydrolysis water removal and distillation of the FFA and readily volatile unsaponifiable components. The distillation residue was additionally hydrolyzed to split the sterol esters into FFA and free sterols, followed by the distillation of the later one.

Accordingly, the problem addressed by the present patented invention was to provide a process for the simultaneous production of tocopherol and sterol which would be applicable to many different starting mixtures, which would not involve the use of toxicologically and ecologically unsafe solvents, which would use even low-concentration starting materials sparingly and which would still give high yields without the use of metal-containing catalysts. In addition, the process would be economically workable on an industrial scale.



*22.5* Process comprising two-step in situ reaction and distillation for purification of tocopherols and sterols as steryl esters from SODDTSC (from Nagao *et al.*, 2005).

Top et al. (1993) described a process for the production of tocopherols and tocotrienols where the PFAD was first modified and the resulting fractions were further purified applying different steps. The process includes the conversion of FFA and glycerides in PFAD into alkylesters by esterification and transesterification, followed by distillation of the resulting product under reduced pressure to remove a major part of the alkyl esters and leave the tocopherols and tocotrienols and other higher boiling point substance in the residue. The residue was cooled to induce crystallization of higher melting substances and other impurities and the crystalline material was filtered off to leave the tocopherols and tocotrienols in the filtrate. The filtrate was further treated by an ion-exchange procedure with a high selectivity anionic resin to produce a concentrated fraction of tocopherols and tocotrienols, the solvent was removed by evaporation. The tocopherols and tocotrienols fraction was washed dried and then subjected to molecular distillation and deodorization to produce a further concentrated product of tocopherols and tocotrienols. After evaporation step, the concentrations of tocopherols and tocotrienols were 83% and 87%, respectively.

In the same invention, an alternative process was described, where the PFAD was pretreated to remove the majority of the FFA by distillation before sending it to the process described above.

Martins et al. (2005) described a process where the SODD was chemically modified, submitted to molecular distillation for fatty acids elimination and the product obtained was submitted to an ethanolic extraction for tocopherols and concentrations of phytosterols. Chemical modification of SODD was conducted by a saponification at 65°C, followed by an acidulation step. With this procedure it was possible to release conjugated fatty acids of acylglycerols molecules. Therefore, not only FFA can be removed from the mixture by molecular distillation, but conjugated fatty acids of acylglycerols also lead to a higher tocopherol concentration. The applied molecular distillation was characterized by using high vacuum, reduced temperature and low residence time. SODD, containing about 75% of FFA, was submitted to four steps of molecular distillation to remove the FFA from the mixture. The separation of tocopherols from sterols was difficult because they have similar molecular weights, boiling points and vapor pressure, and consequently, they are distilling together. Therefore, the resulting product of molecular distillation was submitted to an ethanolic extraction at 0°C to separate the tocopherols from the sterols. As tocopherols are soluble in ethanol, it was possible to separate and to concentrate phytosterols and tocopherols. This process obtained a purity of 26% of tocopherols and 52% of sterols.

A recent patent (Zima *et al.*, 2009) describes a process for preparing a phytolipid composition containing squalene, phytosterols, tocopherols and vegetable wax that consist two steps of distillation at different temperatures and pressure, extraction and precipitation (Fig. 22.6). The final phytolipid product may contain ca. 10% to about 40% squalene, 2% to about 20% phytosterols, 1% to about 10% of mixed tocols and 40% to about 80% vegetable wax with possible applications in the cosmetic, nutraceutical or food industry.



*22.6* Schematic representation of the process for obtaining a phytolipid extract (from Zima *et al.*, 2009).

# 22.4.3 Separation of minor components by solvent extraction

Another method implied for the separation of minor components is solvent extraction, after which the components of interest were further purified by distillation or chromatography (Gunawan *et al.*, 2008). The pretreatment of the feedstock mainly consisted of hydrolysis and neutralization for the concentration of the target minor compound (Chu *et al.*, 2002; Leng *et al.*, 2008). However, esterification was also used to facilitate the separation in polar and non-polar components (Brown and Smith, 1964).

Gunawan *et al.* (2008) reported that the separation results of a modified Soxhlet extraction are comparable to those obtained from molecular distillation. The purpose of their work was to isolate and purify natural FASEs from SODD by a suitable method without degradation of the FASEs.

A modified Soxhlet extraction with hexane was first employed to separate SODD into two fractions based on differences in the polarities of the constituent compounds (Fig. 22.7). The resulting nonpolar lipid fraction (NPLF) was rich in hydrocarbons and FASEs, whereas the polar lipid fraction was rich in FFAs and acylglycerols. The NPLF was then fractionated by a modified silica gel column chromatography to yield FASE-rich fraction. FASEs with high purity were finally obtained by solvent extraction.

By combining a modified Soxhlet extraction, a modified silica gel column chromatography and water/acetone extractions, the FASE fraction with high purity (87%) and high total recovery (85%) could be obtained from SODD with an initial FASE content of 4%. According to the results, this separation process can yield the FASE fraction from SODD without degradation of the FASEs. The advantage of the process is that, starting with SODD, high-purity squalene and FASEs can be obtained. In addition, the polar fraction (PLF in Fig. 22.7) contains



*22.7* Flow chart showing the separation and purification of FASEs from SODD (from Gunawan *et al.*, 2008).

most of the tocopherols and free physterols and can be further processed to obtain pure tocopherols and free phytosterols.

Leng *et al.* (2008) described a process to recover squalene from PFAD using commercial immobilized lipase. The PFAD was hydrolyzed and neutralized, and then squalene was concentrated after a second neutralization and extracted with hexane. In this study, an RSM (response surface methodology) was used to evaluate the effects of several variables (reaction time, water content and lipase concentration) on the enzymatic hydrolysis.

Chu *et al.* (2002) separated tocopherols from PFAD by extraction with hexane after pre-concentration using an enzymatic hydrolysis-neutralization method. Acylglycerols in PFAD were hydrolyzed using a commercial immobilized thermal-stable lipase to liberate FFA and was subsequently treated with alkali. Removal of the FFA salts resulted in concentration of tocopherols. Factors affecting the degree of hydrolysis were studied to reach a better understanding of the recovery of tocopherols from PFAD. It was observed that the FFA levels in PFAD remained unchanged, but the tocopherols concentration decreased when the reaction was prolonged to 7 h. This was explained by the possibility that tocopherols might have been oxidized due to the long period of heating at 65°C. Increase of water content in the reaction mixture from 20% to 50% increased both the FFA levels and tocopherols concentration significantly (p < 0.05). However, a further increase of water content in the mixture significantly (p < 0.05) decreased the FFA levels and the tocopherols concentration.
Winton and Smith (1964) describes a process for the separation of sterols and tocopherols that involves the treatment of DD with a strong acid to convert FFA into esters, followed by the liquid-liquid extraction with a polar and the nonpolar solvent. The obtained polar liquid solution contains mainly sterols and tocopherols and nonpolar liquid solution is rich in esters and TAG. However, under the concept of the invention, there must be a sufficient immiscibility not only of the solvents but also of the solutions formed after admixture of the solvents with the sludge to result in two liquid phases. The process comprised an additional step of separating the polar liquid solution or extract fraction into a sterols product and a tocopherol concentrate. This was obtained by concentrating the solution to the point of incipient precipitation of sterols or complete removal of the solvent by vacuum distillation, followed by crystallization and filtration.

# 22.4.4 Separation of minor components by crystallization and/or use of membranes

Schwarzer and Gutsche (2005) described a process for preparing citrostadienolfree phytosterols. The patented invention relates to a process for the production of phytosterols by alkali-catalyzed transesterification of DD, neutralization of the catalyst and removal of the unreacted alcohol. The phytosterols are crystallized in hydrocarbon by lowering the temperature, optionally after the addition of an adequate quantity of aqueous methanol, and are then removed and purified by filtration, washing and drying. The resulting products have a citrostadienol content of less than 0.5%.

Pan *et al.* (2005) described a method to separate phytosterol and synthesize vitamin E succinate (VES) from rapeseed oil deodorizer distillate (RSDD). The RSDD was esterified with methanol in the presence of sulfuric acid and further cooled to room temperature. After storage at  $-3^{\circ}$ C for 12 h, the esterified RSDD was centrifuged and the precipitate was separated as raw sterols (wet cake). The filtrate was used as the raw material to synthesize VES. The content and total recovery of phytosterol was above 85% and 80%, respectively, after the first crystallization and 95% and 45%, respectively, after the second crystallization.

Isolation of tocopherol succinates from sterol-removed, succinated DD mixture by crystallization was investigated by Lin *et al.* (2007). Membrane technology was also evaluated for its effectiveness to separate tocopherol succinates from mixtures containing sterols and tocopherols. Crystallization was conducted at low temperature with different solvents, including hexane, petroleum ether and a mixture of acetone and methanol (4:1, v/v). The crystallization results showed that recovery of tocopherol succinates from the cake fraction was poor with all solvents tested, with less than 10% of original tocopherol succinates in the raw material being crystallized under conditions employed. Among the solvents tested, hexane was better for the recovery of non- $\alpha$ -tocopherol succinates in the cake fraction. Furthermore, a high property of FFA was co-crystallized along with tocopherol succinates for all solvents used, leading to tocopherol succinates contents in the cake fractions lower than that in the raw material. Two nanofiltration membranes (DS-7 and AP01) were also examined using hexane or petroleum ether as a solvent. The recovery of tocopherol succinates was over 60%. However, their concentration was increased only by 6%. A combined process was then evaluated which include crystallization before succinylation, succinylation, first-stage membrane separation and second-stage membrane separation. The final tocopherols concentration derived from this combined process was as much as that of the original DD.

De Areal Rothes and Verhé (2005) developed a process where acid esterification was applied to corn oil deodorizer distillate (CoDD) in order to increase the ratio of free/esterified sterols that influenced the yield of crystallization. The sterol fraction was further isolated from the FAME by dry fractionation (crystallization). However, more research is required in order to obtain high-purity compounds.

# 22.4.5 Separation of minor components by supercritical CO<sub>2</sub> extraction

In recent years, supercritical fluid extraction using carbon dioxide (SC-CO<sub>2</sub>) has been intensively investigated to some traditional separation techniques, such as vacuum distillation or organic solvent extraction, as an alternative.

Supercritical carbon dioxide extraction is a process where carbon dioxide passes through a mixture of interest at a certain temperature and pressure until it reaches an extractor. This process is used because supercritical carbon dioxide has a low viscosity, a high diffusivity and a low surface tension that provides selective extraction, fractionation and purification, allowing its penetration in micro- and macro-porous materials (Dumont and Narine, 2007).

The major advantage of this method is the easy post-reaction separation of the components by depressurization. Another advantage is the low temperatures used for the majority of the experimentations because carbon dioxide has a critical temperature of 31°C. However, the use of high pressure conditions makes the system energetically expensive but can be economically viable at a rate of production superior to 25% using conditions of approximately 90 atm and 40°C (Mendes *et al.*, 2002). At these specific conditions, only fatty acids are separated from tocopherol (Mendes *et al.*, 2005).

The phase equilibrium data can provide fundamental and necessary information for designing a SC-CO<sub>2</sub> separation process. A number of studies are available for this purpose (Stoldt and Brunner, 1998; Stoldt and Brunner, 1999; Chia-Cheng *et al.*, 2000; Mojca *et al.*, 2003; Pereira *et al.*, 2004).

Simulation and thermodynamic modeling of the supercritical fluid extraction was reported by different authors (Vázquez *et al.*, 2007; Fornari *et al.*, 2009; Martinez-Correa *et al.*, 2010).

Vázquez *et al.* (2007) described a process for the purification of squalene by using CC-SCCO<sub>2</sub>, a by-product obtained after the distillation and ethylation of

olive oil deodorizer distillate (OODD), as raw material. The Group Contribution Equation of State was employed to simulate the separation process and to design the experimental extractions. As satisfactory agreement was found between the experimental and the calculated yields and phase compositions, a raffinate with a squalene concentration of up to 90% was obtained. Finally, the thermodynamic model was employed to develop optimal process conditions to enhance squalene recovery, including partial reflux of the extract product and recirculation of the supercritical solvent in a continuous countercurrent extraction column.

Several authors have studied the concentration of tocopherols directly from the DD, without carrying out any modification pretreatment of the raw material, namely the separation of tocopherols from FFA (Lee *et al.*, 1991; King and Dunford, 2002).

However, the application of pretreatment like esterification leads to two advantageous results for the continuous process, one is that methyl esterified DD (ME-DD) has a higher solubility in SC-CO<sub>2</sub> than DD. The other is that the viscosity is greatly reduced after removing most of the sterols.

The chemical modification of the DD combined with SC-CO<sub>2</sub> has been reported by different authors (Bondioli *et al.*, 1993; Nagesha *et al.*, 2003; Liu *et al.*, 2006; Vázquez *et al.*, 2006; Fang *et al.*, 2007; Vázquez *et al.*, 2007; Torres *et al.*, 2009). In this case, esterification and methanolysis of the DD produced a mixture containing tocopherols, phytosterol esters and FAME, with the process goal of the SC-CO<sub>2</sub> process being the elimination of FAME to concentrate tocopherols and sterol esters in the raffinate.

Lee *et al.* (1991) studied the feasibility of tocopherols concentration from SODD by SC-CO<sub>2</sub> at different temperatures and pressures. It was observed that by increasing the CO<sub>2</sub> pressure, the SODD solubility also increases for all the studied temperature (45°C, 55°C and 70°C) and that esterified SODD has four to six times higher solubility in SC-CO<sub>2</sub> than the sterol-removed SODD. The results showed that SODD initially containing about 13–14% tocopherols may require a countercurrent multistage column to be efficiently concentrated.

King and Dunford (2002) described a solid fluid fractionation method to recover sterol-enriched triglyceride fractions from vegetable oil DD (rice bran and soybean oil DD) using a pilot scale high pressure packed column.

It was possible to obtain oil fractions containing 20–31% sterols and 30–38% TAG, respectively. The method consists of two extraction steps, one carried out at 14 MPa and 45°C and the second extraction was performed at 20 MPa and 80°C. The described method does not leave any solvent or chemical residues in the final product, nor generates additional waste streams requiring subsequent disposal. However, another purification step should be applied in order to obtain a high-purity sterol fraction.

Bondioli *et al.* (1993) described a process to recover squalene from OODD after transformation of the FFA into TAG in order to increase the separation efficiency. OODD was converted into FFA by saponification and splitting. The

mixture was further dried and esterified with glycerol in the presence of an acid catalyst into the corresponding TAG, the latter ones being extracted with SC-CO<sub>2</sub>. The process was carried out on a pilot-plant scale with a column operating in the countercurrent mode. Using this process, squalene was recovered in high purity and yields of about 90%.

Nagesha et al. (2003) described a process where SC-CO<sub>2</sub> extraction of chemically modified SODD was studied at three levels of pressure (180-300 bar) and temperature  $(40-60^{\circ}C)$  to optimize the conditions for enrichment of tocopherols in the raffinate. The modification process includes esterification, saponification, acid hydrolysis and cold crystallization to remove sterols, and again esterification of the FFA obtained from acid hydrolysis of the triglycerides (Fig. 22.8). After modification, SODD containing about 90% of FAME showed improved solubility in SC-CO2 and a better extraction rate. Since FAMEs are more volatile, they were extracted preferentially over tocopherols and other high molecular weight compounds. The extraction at higher pressures and temperatures resulted in a better yield of FAME along with tocopherols and this in turn decreased the degree of enrichment of tocopherols in the raffinate. However, a specific level of pressure and temperature of the extraction caused the increase in the solubility of FAME due to their volatility and results in the enhanced enrichment of tocopherols in the raffinate. It was observed that the enrichment of to copherols (36%) to ten times the original concentration of the feed (4%)occurred at an extraction pressure of 180 bar and a temperature of 60°C.

The recovery of tocopherols and sterols from sunflower oil deodorizer distillates (SfODD) using countercurrent supercritical carbon dioxide extraction (CC-SCCO<sub>2</sub>) has been studied by Vázquez *et al.* (2006). The chemical transformation of the SfODD composition significantly enhances the concentration of minor lipids in the raffinate product. This pretreatment resulted in a mixture (ethylated SODD) which mainly consists of tocopherols, sterols and fatty acid ethyl ester (FAEE). Additionally, the reaction step produced a solid phase, mainly consisting of sterols, which was isolated from the liquid product.

After two consecutive extractions with hexane, the sterol purity in the new solid phase increased up to ca. 88%, which corresponds to 18% of recovery of the total sterols present in the original SODD. A similar procedure was accomplished replacing hexane by ethanol. In this case, the purity of the sterols obtained was similar, although the recovery was reduced to ca. 10%. This low value of recovery indicates a higher solubility of the sterol solid phase in ethanol compared to that in hexane.

The main drawback of the CC-SFE process described in the present study is related to the high amount of unidentified compounds present in the original SODD (20%). Around 50% of this unidentified material corresponds to non-volatile compounds which preferably accumulated in the raffinate.

 $CC-SCCO_2$  extractions of the ethylated and original SODD resulted in a 3.7-fold increase in the tocopherol + phytosterol concentration (ca. 80% recovery)



*22.8* Schematic representation of the chemical modification process of SODD (from Nagesha *et al.,* 2003).

with the ethylated material, while only a 1.3-fold increase was obtained with the original SODD.

Additionally, during the formation of FAEE, partial crystallization of free sterols occurs, and around 20% of the sterols present in the original SODD can be recovered with high purity (88%) in the solid phase.

Liu *et al.* (2006) studied the vapor-liquid phase equilibrium data for  $SC-CO_2$  and methyl esterified DD (ME-DD) at 40°C and in the pressure range of

9.7–16.2 MPa in order to determine the feasibility of SC-CO<sub>2</sub> to concentrate natural tocopherols from SODD. The results showed that the separation factor between tocopherols and FAME was from 2.5 to 3.8 at 40°C and 9.7–16.2 MPa, which is fundamental and necessary for future process designs. For this purpose a modification process of DD was applied that includes esterification, cold crystallization for removing sterols and alcoholysis. The FFAs obtained from TAGs by alcoholysis were further esterified to FAMEs. The detailed procedure is shown in Fig. 22.9. Through such pretreatment, the obtained methyl esters (ME-DD) contained 52% FAME and 8% of tocopherols and other compounds. After the reactions, most of the sterols were easily removed because of their low solubilities in FAMEs below 4°C.



*22.9* Oil deodorizer distillates (DD) modification process (from Liu *et al.*, 2006).

Fang *et al.* (2007) described a process where SC-CO<sub>2</sub> fractionation was employed to concentrate tocopherols from ME-DD. The initial pressure, feed location, temperature gradient and ratio of CO<sub>2</sub> to ME-DD were optimized for separating FAMEs. For the following tocopherol concentration step, a final pressure of 20 MPa resulted in the greatest average tocopherol content (>50%) and tocopherol recovery (about 80%).

ME-DD was prepared from DD through the pretreatment process that include two steps of esterification and methanolysis, which converted FFA and glycerides into FAMEs. The two reactions were conducted with the catalysts of sulfuric acid and sodium methoxide, respectively. After each reaction, the mixture was washed until neutral. Finally, the mixture was stored in a refrigerator for 12 h. As a result most of the sterols were crystallized and removed by filtering under reduced pressure. A fractionation column was required for the ME-DD separation. Low pressure (the initial pressure) was used in combination with a temperature gradient along the column to separate the FAMEs. Then, the pressure was increased to separate the tocopherols from other impurities.

Torres *et al.* (2009) reported a two-step enzymatic reaction to obtain phytosterol esters, where the SODD was initially modified by the addition of oleic acid in order to decrease the DD melting point. After esterification steps, the product obtained comprised mainly FAEEs, tocopherols and phytosterol esters, together with minor amounts of squalene, FFAs, free sterols and triacylglycerols. The FAEEs were eliminated by SC-CO<sub>2</sub> and the phytosterol esters and tocopherols were concentrated in the raffinate. The separation between the last two compounds was carried out in an isothermal countercurrent column (without reflux), with pressures ranging from 200 bar to 280 bar, temperatures of 45–55°C and solvent-to-feed ratios from 15 kg/kg to 35 kg/kg. Using these extraction conditions, the fatty acid esters were completely extracted. The phytosterol esters were concentrated in the raffinate up to 82% with a yield of 72%.

# 22.4.6 Separation of minor components using urea

Sampathkumar (1986) described a process for recovering tocopherols from deodorizer sludge for use in pharmaceutical and food applications without the loss of vitamin E activity with an overall yield of 97%. It was found that urea forms an inclusion complex with all the fatty acids and glycerides of fatty acids without entrapping the sterols, tocopherols and other bulky molecules present in the deodorizer sludge or distillate.

The process comprises the heating of deodorizer sludge and a solution of urea mixture to form a urea complex of the fatty acids and glycerides of fatty acids. The mixture was cooled to precipitate the urea complex from the mother liquor containing the tocopherols, and separating the mother liquor from the precipitate. The mother liquor was further concentrated and the residual solids were separated. Extracting the mother liquor, an oil rich in tocopherol could be obtained. It was suggested that the instability of the urea complex of fatty acids in the presence of water and an acid can be used for further purification of FFA and their separation.

A similar process was described by Maza (1992) where urea was used for the separation of mixed fatty acids, sterols and tocopherols from DD with an increased yield and reduced use of organic solvents. The process comprised the sequential steps of (1) melting the DD, (2) adding the melted DD to a refluxing solution of urea and alcohol to form a mixture, (3) mixing the reaction mixture while cooling to allow formation of crystals, (4) separating the crystals, (5) drying the crystals, (6) dissolving the crystals in water to form an organic layer which is rich in mixed fatty acids and an aqueous layer containing urea and (7) separating the fatty acid layer. By applying this process, a light fraction enriched in FFA and a heavy fraction enriched in tocopherols and sterols were obtained. Urea is recovered for reuse by combining the separated aqueous solutions containing urea and evaporating the water. The key element of the invention is the first step of the process, i.e. melting of the DD providing an easily dispersed reactive liquid which is not diluted in the solvent.

### 22.4.7 Separation of minor components by adsorption

Chu *et al.* (2004) separated tocopherols from PFAD using silica in a stirred batch adsorption reactor. The equilibrium of the adsorption process as a function of the reaction temperature, the agitation rate and the silica mass on tocopherols adsorption onto silica was investigated over a concentration range of tocopherols. A lower reaction temperature led to a higher tocopherols uptake at equilibrium, indicating that the adsorption process in this study was exothermic. The adsorption capacity increased with the rise in agitation rate. However, in this study the maximum adsorption capacity remained unchanged when the silica mass was increased. The thermodynamic parameters of the adsorption process helped in predicting how the retention of vitamin E might vary with a temperature change. However, information on the separation performance, such as tocopherols recoveries, is not available.

Fabian *et al.* (2009) described a new approach for the separation of a NPLF from SODD using a stirred batch-wise hexane desorption to achieve the same degree of separation as that obtained by a modified Soxhlet extraction that was reported in a previous study by Gunawan *et al.* (2008). The effects of the operation parameters, such as the silica gel to SODD mass ratio, the solvent volume to SODD mass ratio and the adsorption-desorption temperature on separation, were systematically investigated. Starting with SODD that contains 4% FASEs, 2% squalene, 13% tocopherols and 9% free phytosterols, it was possible to obtain an NPLF enriched with FASEs (19%, recovery 97%) and squalene (9%, recovery 100%). The contents of FFAs, TAGs, tocopherols and free phytosterols remained in the NPLF were 12%, 1%, 5% and 1%, respectively. In addition, the NPLF contained squalene and FASEs that could be processed further to obtain pure squalene and FASEs as described in the previous work (Gunawan *et al.*, 2008). The batch extraction employed in this study yielded about the same degree of

separation as compared to that of modified Soxhlet extraction. However, the advantage of the method of this study is that it can be scaled-up easily.

### 22.5 Future trends

Economic consideration is a key driving force behind the development of the technologies to process inexpensive biodiesel feedstocks and to recover the minor components.

The purification of minor components from DDs is a complex process that implies multiple steps and techniques. When a desired material is produced industrially, the way of processing affects the cost of production. Therefore, in order to make a process industrially viable, the number of steps has to be reduced. However, their valorization should be considered when the DD from chemical refining is used for the production of biodiesel.

There are different routes (direct conversion or acylglycerol route) to convert the DDs to biodiesel/biofuel, some of which have found industrial application. A pretreatment of the feedstock or post-treatment of the final biodiesel are necessary in order to meet the quality specifications.

A combination of technologies opens broad opportunities to convert low-price lipid resources into biodiesel/biofuel that complies with the EU and ASTM specifications and to valorize minor components for different applications.

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# Utilisation of biofuels in diesel engines

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**Abstract:** This chapter summarises findings on the use of biofuels in conventional diesel engines. A number of biofuels such as vegetable crude oil, pure plant oil and biodiesel in different forms, which are derived from many types of raw materials such as jatropha, coconut, palm, kapok nut and cat-fish, are investigated to find the impact of these biofuels on the engine's combustion characteristics, performance, exhaust emissions and durability. The concept of using biofuels in engines is also mentioned to determine ways of utilisation of biofuels in engines that match both the demands of biofuels use and the design of the engines.

**Key words:** biofuels utilisation, engine performance, exhaust emission, durability.

#### 23.1 Introduction

Biofuels are now recognised as the most suitable alternative fuels for engines which were originally designed to use fossil fuels. Although the process of formation of fossil fuels still continues through the effect of underground heat and pressure, the current rate of consumption is higher than the rate of formation. Consequently, fossil fuels are considered to be non-renewable, that is, they are not replenished as fast as they are consumed. Biofuels, including ethanol, biodiesel and several other liquid and gaseous fuels, constitute a very promising renewable energy resource with the potential to displace the consumption of a substantial amount of petroleum worldwide during the next few decades.<sup>1–4</sup> A clear trend in that direction is already in process.

Research on the production and utilisation of biofuels in engines is therefore regarded as a priority not only for developed nations but also for developing countries. Although the use of biofuels is currently low, the amount is continuously increasing in every country. However due to the fact that biofuels are produced from many different sources, characteristics and quality also vary, so the utilisation of different biofuels in internal combustion engines must be carefully investigated to determine the effects on engine performance and material components.

In this chapter the utilisation of biofuels in conventional diesel engines is considered. The use of crude jatropha oil (CJO), degummed jatropha oil (DJO), pure plant oils (PPOs), and biodiesels produced from crude palm oil (CPO), *Jatropha* 

*curcas*, coconut oil, kapok nut oil and cat-fish fat in neat form (100% biodiesel) together with various blends of biodiesel with conventional diesel is described. In addition, the use of mixed biodiesel derived from different raw materials is also considered as a possible solution for improving the quality of biodiesels.

Findings regarding the utilisation of biofuels in diesel engines are presented from case studies conducted in ASEAN (Association of Southeast Asian Nations) countries, especially Indonesia, Thailand and Vietnam, where high priority has been given to the development and use of biofuels.

# 23.2 Utilisation of vegetable pure plant oil and crude oil in diesel engines

#### 23.2.1 Introduction

Early in the research stage CJO was considered to be suitable as a fuel oil based on its visual properties. The greatest difference between CJO and diesel oil is in viscosity. The high viscosity of CJO may contribute to the formation of carbon deposits in Compression Ignition Engines (CIE). Incomplete fuel combustion results in reduced engine life. Reducing the viscosity of CJO oil by preheating or dilution with diesel fuel was studied in engine tests.<sup>6,24</sup> To investigate the suitability of CJO oil as alternative fuel and examine emissions, two tests of performance and exhaust gas emission, and a long-term durability test of CIE in a direct injection (DI) engine were conducted. In performance and exhaust gas emission tests, JO10 (blend of 10% CJO and 90% diesel) was similar to diesel fuel. Its oxygen content is an advantage in improving combustion. Exhaust gas emission increased slightly because its slightly higher viscosity influences fuel atomisation. JO10 is a promising alternative fuel because its performance and exhaust gas emission are similar to diesel fuel. JO100 gave lower performance and higher emission compared to diesel fuel because of its high viscosity. Using JO100 the engine was difficult to operate. The long-term durability test indicated that JO10 resulted in operational problems including increased exhaust gas emission (HC, particulate matter), injector coking, piston and liner erosion. Maintenance frequency would be increased substantially including changing or cleaning of the injector nozzles at 125 hour intervals, thus increasing the cost of operation. Dilution of lubricating oil and friction caused by ring sticking and deposits in the combustion chamber would reduce the lifetime of engine components. The main concern is the fuel quality and composition. The content of phosphorous compounds in JO10 was found to be significant affecting the combustion process and exhaust emission. A degumming process to reduce the phosphorous level is therefore required to improve the fuel quality of CJO.

Diesel engines can be operated on either PPO or biodiesel. The biodiesel process increases the cost of production as many processes are needed, whereas PPO only needs degumming to decrease phosphorous content and deacidification to decrease acid number. Potential resources of PPO in Indonesia include coconut, palm and jatropha as they are tropical plants with a high population throughout the country. Various PPOs have been investigated.<sup>7,8</sup> Test fuels include pure coconut oil (PCO), pure palm oil (PPaO), pure jatropha oil (PJO)<sup>9</sup> and diesel fuel for comparison. Each PPO was blended with diesel fuel with composition 50%-volume and heated to 60°C, to decrease the viscosity by 1/10. Trials using a small DI diesel engine for 17 hours endurance tests under various operating conditions were conducted according to engine test bed procedures for DI diesel and engine injector nozzle coking test. PPOs are characterised by high viscosity, low volatility and low energy content. All PPOs had higher brake specific fuel consumption (BSFC) before the endurance test by comparison with diesel fuel, but at the end of the test all PPOs had BSFC similar to diesel fuel due to decreased friction between engine components. However combustion of PPOs was not as complete as that of diesel fuel because of poorer spray characteristics, evidenced by low CO2 and high UHC, carbon monoxide (CO), O2 and opacity emissions. The phosphorus content, unsaturated fatty acid content and low combustion quality of PPO result in higher engine deposits than for diesel fuel. Even though the PPOs had been degummed the residual phosphorous content contributed to deposit formation. Deposits from PPOs were between 140% and 290% more than from diesel. However PPOs exhibited anti-wear properties on the plunger and injector due to the lubrication effects of the fatty acid content. PCO had the best anti-wear property of the test fuels.

Further investigation of the combustion and exhaust gas emissions of a DI CIE using *Jatropha curcas* L. oil as CJO (JO) and PJO/Degummed Jatropha Oil (DJO) was done.<sup>10</sup> Of all the tested fuels, DJO10 was found to be closest to diesel fuel in performance, exhaust gas emission and its combustion process (ignition delay).

In addition a study of combustion of *Jatropha curcas* L. oil (crude, degummed, fatty acid methyl ester) as a fuel in a DI diesel engine was conducted.<sup>11,12</sup> The summary of conclusion drawn from the experimental data was as follows:

- JO100 and DJO100 have low cetane indexes and very high viscosity. Lower engine performance and high exhaust gas emission were found. However, these fuels can be used in emergencies.
- Blends of JO10 and DJO10 improve engine performance and reduce exhaust gas emissions at low engine load. However, nitrogen oxides (NO<sub>x</sub>) emission tends to increase.

# 23.2.2 Combustion visualisation

#### Combustion bomb study

The study on the spray combustion characteristics of 10% CPO blended with diesel fuel was conducted in a constant volume combustion chamber. With the fixed experimental conditions such as spray ambient pressure and injection events, the effects of 10% CPO diesel at the injection line pressure of 100 MPa on spray

combustion and flame structure were investigated using photo diode and ICCD camera. The two-colour method was also employed to predict combustion flame temperatures and KL factors.

The injection system used in this research was an electronically controlled accumulator type fuel injector system.<sup>13,14</sup> With a 0.2 mm diameter single hole injector, driven by a piezo electric actuator via an extended pressure pin, we could control the needle lift and fuel injection rate shaping. The schematic diagram of the injector and details are shown in Fig. 23.1.

Experiments were conducted in a constant volume 2.2 litre vessel with 80 mm diameter quartz observation window on the side, gas mixing propeller on the bottom and injector on the top, as shown in Fig. 23.2. The ambient conditions maintained inside the vessel were high temperature and pressure by igniting hydrogen in an enriched oxygen and air mixture. The oxygen concentration after the hydrogen combustion was approximately 21% by volume.<sup>13,14</sup>

The rectangular injection rate shaping was obtained in this experiment, as shown in Fig. 23.3. Fuel injection mass was set at approximately 15 mg for all experiments. Injection pressure was 100 MPa. The fuel was injected in the vessel at the ambient conditions of 3.0 MPa, temperature around 900°C, as shown in Fig. 23.4. The calculated composition of ambient gas was  $O_2 20.9\%$ ,  $N_2 70.8\%$  and  $H_2O 8.3\%$ .



23.1 Schematic diagram of the injector system.14



23.2 Experimental apparatus.



23.3 Fuel injection rate shaping at an injection pressure of 100 MPa.<sup>15</sup>

After the hydrogen combustion, the fuel was injected into the vessel and then combusted. Fuel spray combustion flame photographs were taken by ICCD camera. Light emission of flame was measured using two photo sensors: a photo multiplier tube with a band-pass filter centres on a wavelength of 310.3 nm (FWHM: 16.3 nm) was used for measuring the intensity of OH radical emission and two photo diodes (used for measuring the luminous light intensity) at the upper and the middle of observation window. The start of spray was detected by the combination of the use of He-Ne laser with photo sensor. Using photo diode data, then the ignition delay and combustion period were evaluated.



23.4 Temporal variation of gas pressure inside the vessel.<sup>15</sup>

The two-color method was applied to estimate two dimension (2D) contour of temperature and KL factor (KL factor is the factor used to indicate soot) distribution in the combustion flame. This two-colour pyrometry system was set up by placing Vari lens that has the two-different band-pass filters 488 nm in centre wavelength (FWHM: 11.3 nm) and 634 nm in centre wavelength (FWHM: 8.5 nm) for separating image to be two in front of an ICCD camera lens. The intensity data of both filters were used to calculate the true temperature and KL factor.

The data obtained from He-Ne laser and OH-radical were used to calculate ignition delay. It was found that 10% CPO diesel gave shorter ignition delay compared with diesel as shown in Fig. 23.5.

The data 10% of peak intensities obtained from the two photo diodes were selected to be the start and end of the combustion. The result shows that the observed combustion period of 10% CPO diesel at injection pressure of 100 MPa was slightly shorter than diesel as shown in Fig. 23.6.

The amount of injection fuel became slightly smaller and the injection period became slightly shorter with the 10% CPO diesel due to the higher viscosity of 10% CPO diesel.

The exposure time of ICCD camera was set at 10 µsec.<sup>15</sup> The spray combustion flame intensity data complied with two colour method.<sup>16</sup> Some of the calculated results of true temperature are shown in Fig. 23.7.

The calculated data obtained from spray combustion flame true temperature were used for calculating the KL factor, the factor for indicating amount of combustion soot in flame. The calculated results are shown in Fig. 23.8.



23.5 Fuel combustion ignition delay.<sup>15</sup>



 $23.6\,$  Fuel spray combustion period with injection pressure of 100 MPa at ambient conditions of 3 MPa.  $^{15}$ 

Total KL factor is the summation of KL factor over the spray combustion flame area. This factor could be used to estimate the total soot of the combustion.

It was found, as shown in Fig. 23.9, that the difference in total KL factor between diesel and 10% CPO was very small.

The average KL factor, shown in Fig. 23.10, was calculated from the total of KL factor divided by spray combustion flame area at all flame area. This factor could be used to estimate the soot concentration of the spray combustion. The



23.7 Spray combustion flame temperature distribution.



23.8 KL factor distribution.



*23.9* Total KL factor of palm diesel 60% and diesel fuel at an injection pressure of 100 MPa and 60 MPa.



*23.10* Average KL factor of palm diesel 60% and diesel fuel at an injection pressure of 100 MPa and 60 MPa.

results have shown that the difference of average KL factor between diesel and 10% CPO was very small.

Histograms of temperature and KL factor were calculated by evaluating the value from the counted number of spray combustion flame pixel and converting them to flame area (mm<sup>2</sup>). The interval of temperature and KL factor were selected at 50 K and at 0.005 A.U., respectively. The results are shown in Fig. 23.11.



*23.11* Flame temperature and KL factor histogram of palm diesel 60% and diesel fuel at an injection pressure of 100 MPa and 60 MPa.

It was found from temperature histogram that spray combustion of 10% CPO started with lower temperature than diesel. Spray combustion temperature had increased close to diesel during the mid range of combustion period. Then, it became lower by the end of combustion. However, the differences were very small.

The KL factor histogram of Thai palm 10% CPO had no significant difference compared to diesel. Hence, it could be concluded that the difference in soot emission could be very small.

The effects of 10% CPO diesel at an injection pressure of 100 MPa on spray combustion and flame structure were investigated. It was found that diesel blending with 10% CPO has shorter ignition delay and shorter combustion period compared with conventional diesel fuel. High temperature combustion area (over 2400 K) of 10% CPO diesel was also smaller than diesel, especially at the end of the combustion period. The amount of soot and soot concentration affected by this blending percentage may not be significantly different from the diesel fuel.

#### Combustion engine study

The combustion engine study aims to investigate comparative results of using crude palm diesel (blending 10% of CPO in diesel, 10% CPO diesel) on engine combustion of a CI IDI swirl chamber engine. The experiments, conducted on a Ford Ranger WL81 2.499 litre engine, were composed of two parts. First, measure and analyse in-cylinder pressure and fuel injection line pressure by using crude palm diesel and diesel fuel. Second, study combustion phenomena of both fuels in the swirl chamber by means of engine visioscope. Results show details of phenomena of spray, flame propagation. Two-colour method was also employed to evaluate flame temperature and distribution of soot in flame. And finally, to compare results of visualised combustion phenomena with heat release that estimated from in-cylinder pressure information.

Many properties of the 10% CPO diesel fuel can be attributed directly to the thickening effect of the CPO on the diesel fuel. In this study, blending 10% of CPO by volume in diesel can meet the Thai diesel fuel specification. The primary properties of both the baseline diesel and the crude palm diesel blend are shown in Table 23.1. The higher density and higher viscosity of CPO compared with diesel fuel resulted in slight increasing of these properties in the resulting crude palm diesel blends. The blend also has roughly 5% less energy per volume and less cetane value than diesel fuel. The 10% CPO diesel shows the slight reductions in T90 point that may affect the poor long-trip economy. The addition of CPO to diesel fuel will degrade the cetane number of the resulting 10% CPO diesel blend. The flash point of 10% CPO diesel is controlled by high flash point of the CPO. The flash point of 10% CPO diesel is higher than that of diesel fuel.

The engine under study is a commercial IDI, water cooled four cylinders, in-line, natural aspirated engine. The following chart displays the main dimensions:

Engine type	WL 81
Pre-chamber	Swirl pre-chamber
Displacement	2499 cm <sup>3</sup>
Bore	93 mm
Stroke	92 mm
Compression ratio	21.6
Injection pump	Rotary distributor type
Injector starting pressure	11.4–12.1 MPa

Properties	Unit	Test method	Reference diesel	10% CPO diesel	Thailand diesel specification
Specific gravity @ 15.6/15.6°C		ASTM D1298	0.8266	0.8360	0.810–0.870
Cetane index		ASTM D976	58.9	_	47 min
Cetane number		ASTM D613	59.3	55.5	47 min
Viscosity @ 40°C	CST	ASTM D445	3.10	3.910	1.8–4.1
Pour point	°C	ASTM D97	-3	-6	10 max
Distillation		ASTM D86			
IBP	°C		_	_	_
10% recovered	°C				_
50% recovered	°C		_	_	_
90% recovered	°C		350.6 522	346.2	350 max
Lubricity by HFRR	μm	CEC F-06-A-96	(+LA = 398)	209	460 max
Total acid number		ASTM D974	0.04	1.02	_
Gross heating value	J/g		45968	44982	44500 min

Table 23.1 Comparative diesel and 10% CPO diesel properties<sup>17</sup>

The engine was connected to an AVL alpha 40 eddy-current dynamometer. In-cylinder pressure was taken by AVL piezoelectric pressure transducer model GU12P. Fuel line pressure was taken by a KISTLER 607C1 pressure transducer.

Indicating data were captured with Cussons P4503 shaft encoder and Cussons P4500 autoscan. Direct photography was taken with an AVL Engine Visioscope. The system consists of a PixelFly VGA Colour CCD camera (resolution 640 × 480 pixel), an AVL control unit, AVL 364C crank angle encoder, an optical linkage to the camera and the endoscope. The optical access for the endoscope to the swirl chamber of the fourth cylinder was prepared through the cooling system of the cylinder head. The visioscope software controls the triggering of the digital camera within a crank angle tolerance of  $0.1^{\circ}$ CA. The endoscope has a viewing angle of 30° forward view. To capture the spray images, the light source unit with fibre optic (40 mJ/flash with 20 µs duration at frequency of 10 Hz) was used.

The schematic arrangement of experimental set up is shown in Fig. 23.12.

The experiments were carried out at constant speed, steady state conditions at selected high probability operating points along ECE 15 driving cycle, as shown in Table 23.2.<sup>17,18</sup> For the combustion analyses, images of simultaneous complex spray, inflammation and combustion processes in the swirl chamber were taken. Speed, torque, fuel consumption, engine operating pressure and temperature for both fuels were recorded during each test.

Comparison of in-cylinder pressure, fuel line pressure, fuel injection rate, heat release rate, net heat release and mass fraction burned is shown in Fig. 23.13.<sup>18</sup> The measurement of in-cylinder pressure and fuel injection line pressure has



23.12 Schematic arrangement of experimental system.<sup>17</sup>

Table 23.2 Engine test point	s (selected high probability	operating points	along ECE
15 driving cycle)			

Test point number	Speed (rev/min)	Torque (Nm)	Statistical frequency (%)
1	ldle s	beed	39.49
2	1000	30	2.05
3	2000	30	7.69
4	2000	50	n.a.
5	2250	20	1.02
6	2750	20	12.31

indicated that 10% CPO diesel has approximately 1° of early injection timing compared with diesel. The 10% CPO diesel also has longer ignition delay and higher amount of fuel injected mass ( $m_f$ ) due to its lower energy density. The maximum in-cylinder pressure of 10% CPO diesel is similar to diesel. Net heat release and mass fraction burned of 10% CPO diesel are also lower than diesel.

Comparison of maximum in-cylinder pressure  $(P_{max})$ , SOI, ignition delay and fuel injected mass  $(m_f)$  as engine operates with diesel and 10% CPO diesel are summarised in Table 23.3.



*23.13* Comparison of in-cylinder pressure, fuel line pressure, fuel injection rate, heat release rate, net heat release and mass fraction burned as engine operates with diesel and 10% CPO diesel at 2000 rev/min, 30 Nm.<sup>18</sup>

	P, (b	<sup>max</sup> ar)	SO (°C,	l A)	lgnition (µsec)	delay	m <sub>f</sub> (mg/c	ycle)
Test point	Diesel	10% CPO diesel	Diesel	10% CPO diesel	Diesel	10% CPO diesel	Diesel	10% CPO diesel
Idle 1000 rpm, 30 Nm	53.26 58.45	53.31 59.45	-4.0 -10.5	-4.0 -11.5	2.08 2.08	2.2 2.17	6.22 9.63	7.04 10.77
2000 rpm, 30 Nm	61.48	61.84	-11.0	-11.5	1.54	1.50	9.99	10.88
2000 rpm, 50 Nm	61.72	61.74	-10.0	-10.0	0.46	0.46	12.64	13.97
2250 rpm, 20 Nm	64.98	64.97	-10.5	-11.0	0.78	1.04	8.72	9.81
2750 rpm, 20 Nm	63.90	64.66	-9.0	-9.0	0.21	0.21	9.56	10.46

*Table 23.3* Comparison of maximum in-cylinder pressure ( $P_{max}$ ), SOI, ignition delay and fuel injected mass ( $m_f$ ) as engine operates with diesel and 10% CPO diesel<sup>18</sup>

The images of spray formation at selected operating points of reference diesel and 10% CPO diesel are shown in Fig. 23.14 (a) and (b), respectively.<sup>17,18</sup> The figures show that 10% CPO diesel has approximately 1°–2° of early injection timing compared with diesel. The early injection timing is probably due to the higher isentropic bulk modulus and higher viscosity of CPO compared with diesel, resulting in a slight increase in these properties in the resulting blends.<sup>19</sup> The comparison of the observed spray formation between reference diesel and 10% CPO diesel are summarised in Table 23.4. It was found that, using OEM injection pump and standard injector in a pre-chamber, with 10% CPO diesel the observed sprays were wider than that of reference diesel. The difference in spray angle tends to reduce with increasing speed. The observed spray penetration with 10% CPO diesel is also longer than reference diesel in low to medium engine speed range. The higher the engine load, the longer the spray penetration was observed.

Summarising the results of these sections, as shown in Fig. 23.15, it can be noted that the visible combustion course in a swirl chamber occurs without any starting aids.<sup>17,18</sup> The visible inflammation appears above the fuel jet. From there the flame engulfs the whole swirl chamber very quickly. This process needs some delay times. The comparison of the observed luminous spray combustion between reference diesel and 10% CPO diesel is shown in Table 23.5. It was found that 10% CPO diesel has shown a longer ignition delay period than diesel. The combustion for both fuels tends to start faster with increasing speed. After this ignition delay, the burning area rotates under the influence of the swirl. This motion can be observed for nearly the entire burn duration after complex luminous inflammation has occurred. In the low speed and load range, 10% CPO diesel



(b) 10% CPO diesel.

*23.14* (a) and (b) Images of liquid fuel spray in the pre-chamber for reference diesel and 10% CPO diesel respectively. The crank angles at which the images were acquired are written on the left of the images.

Table 23.4 Maximum s	pray penetration (m	m) and spray angle	(degree)
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	Maximum (mm)	penetration	Maximum (degree)	Maximum spray angle (degree)		
Test point	Diesel	10% CPO diesel	Diesel	10% CPO diesel		
ldle	23.0	27.8	25.5	24.1		
1000 rpm, 30 Nm	27.9	25.6	24.1	26.4		
2000 rpm, 30 Nm	29.8	27.1	36.8	41.4		
2000 rpm, 50 Nm	28.3	28.7	36.3	39.3		
2250 rpm, 20 Nm	25.6	28.4	36.4	39.4		
2750 rpm, 20 Nm	28.5	33.7	36.4	40.8		



<sup>(</sup>b) 10% CPO diesel.

*23.15* Images of luminous spray combustion in the pre-chamber for reference diesel and 10% CPO diesel showing the start of luminous flame, the position for maximum area of over 2400 K and end of luminous flame. The crank angles at which the images were acquired are written under the images.

combustion duration tends to have a slightly shorter period than diesel. This may be due to the benefit of oxygen content in the fuel.

Using the 'Thermovision' software from AVL List GmbH,<sup>20</sup> the temperature of radiating soot particles was calculated from the three spectral intensities in the flame images using the two-colour method. In the temperature images, shown in Fig. 23.16, purple – blue – green – yellow – red – white in the original colour image denote the temperatures ranging from 1800 to 3000 K.

Table 23.5 Comparison of the first appearance of luminous flame, end of luminous
flame and luminous flame duration between reference diesel and crude palm diesel
in an IDI engine

	First appearance of luminous flame (°CA)		End of luminous flame (°CA)		Luminous flame duration in pre-chamber (°CA)	
Test point	Diesel	10% CPO diesel	Diesel	10% CPO diesel	Diesel	10% CPO diesel
Idle 1000 rpm, 30 Nm 2000 rpm, 30 Nm 2000 rpm, 50 Nm 2250 rpm, 20 Nm 2750 rpm, 20 Nm	3.5 0.5 -0.5 0.5 -0.5 1.0	5.0 2.0 -0.5 -0.5 -0.5 -1.0	28.5 32.5 30.5 27.5. 25.5 27.5	25.5 31.0 28.5 31.0 27.0 26.5	25.0 32.0 31.0 27.0 26.0 26.5	20.5 29.0 29.0 31.5 27.5 27.5



(a) Diesel.

*23.16* Flame temperature images of spray combustion in the prechamber for reference diesel and 10% CPO diesel. The crank angles at which the images were acquired are written at the top of the images.

(Continued)



(b) 10% CPO diesel. 23.16 Continued.

The difference in combustion is much more obvious when looking at the flame. The in-cylinder combustion temperature of 10% CPO diesel combustion is lower than diesel combustion. From Fig. 23.17, the flame areas of temperature above 2400 K for diesel and 10% CPO diesel at 2000 rev/min, 30 Nm are compared. It was found that diesel fuel showed greater amount of flame areas of temperature above 2400 K.

In the soot distribution images, the same colour scale denotes soot densities ranging from thin to dense soot. The appearance of luminous combustion flame comes from the radiation of soot particles occurred in the fuel mixture oxidation zone. Prediction of soot density distribution at selected operating points of diesel and 10% CPO diesel are shown in Fig. 23.18. It is noted that soot density in 10% CPO diesel combustion flame tends to be slightly lower than that in diesel.

Comparative studies of engine fuelled with reference diesel and 10% CPO diesel were investigated. Visualised images show the effects of CPO in 10% CPO diesel blend. The injection timing of 10% CPO diesel is approximately 1° earlier compared with the injection timing of reference diesel. Observed 10% CPO diesel fuel sprays have shown either longer spray tip penetration length or wider spray angle than the reference diesel.



23.17 Flame area with temperature above 2400 K for 10% CPO diesel and diesel at 2000 rev/min, 30 Nm.



(a) Diesel.

23.18 Soot concentration distribution images of spray combustion in the pre-chamber for reference diesel and 10% CPO diesel. The crank angles at which the images were acquired are written at the top of the images. (Continued)



(b) 10% CPO diesel. 23.18 Continued.

Images of spray combustion indicate that the period of 10% CPO diesel combustion phenomena occurred more retardedly with respect to TDC than diesel. As its consequence, together with the lower heat of combustion, the predicted combustion flame temperature and soot density distribution, using the two-colour method, are lower than the reference diesel. The combustion for both fuels tends to start faster with increasing speed. The observed combustion duration of 10% CPO diesel is slightly shorter than that of diesel.

# 23.3 Utilisation of biodiesel based palm oil, jatropha oil, coconut oil and kapok nut oil in diesel engines

Palm (*Elaeis guineensis*) is the most potential source of edible oils. Palm oil is now already produced and marketed in very large quantities, because it is edible and is high yielding (+/-3 ton/hectare/year). Direct injection (DI) diesel engine performance,

exhaust gas emissions and some of fuel properties have been studied for biodiesel from CPO and Refined Bleached Deodorized Palm Oil (RBDPO), and these fuels blended with diesel fuel.<sup>21</sup> It was found that both of biodiesel fuels and their blended fuels with diesel oil had increased BSFC levels, while the exhaust emissions (CO, CO<sub>2</sub>, HC and smoke) were better than for diesel fuel. Both DI and IDI<sup>22</sup> engines were used for this research. These fuels were also used for a 2200 km fleet road test with two passenger cars and two trucks and compared with the performance of neat petrodiesel fuel.<sup>5</sup> Parameters evaluated before and after road testing were fuel consumption, exhaust gas emissions, fuel injection equipment and engine lubricant.

Physic nut (*Jatropha curcas*) is one of the most potential sources of non edible plant oil. Physic nut seed oil is practically unexploited commercially, although it has the potential to replace or substitute palm oil as the raw material for biodiesel during the periods of high food sector demand.

The effect of biodiesel fuel from *Jatropha curcas* oil in DI diesel engines on the components of the engine influenced by fuel before (injection pump, injector) and after the combustion process (piston crown, cylinder head) was studied.<sup>23,25</sup> The test bed procedure used was that commonly used for injection cleanliness evaluation adopted by World-Wide Fuel Charter (December 2002).<sup>26</sup> Exhaust gas emissions such as NOx, CO, BSFC and engine lubricant before and after the test were also measured.

A single cylinder DI diesel engine fuelled with pure biodiesel from physic nut oil and blends (B10, B20, B50) with diesel fuel was used to compare engine performance and engine exhaust gas emission by comparison with diesel fuel.<sup>27</sup> The results from this research show that biodiesel fuel from physic nut oil and its blends with diesel can give comparable engine performance for parameters torque (T), fuel volumetric consumption (FVC), brake specific energy consumption (BSEC) and thermal efficiency ( $\eta$ e). Engine exhaust gas emissions of total hydrocarbon (THC), CO and smoke emissions were reduced significantly when engine was run with biodiesel fuel. Biodiesel use resulted in slight increases of NOx emission.

Much research has been focused on the use of biodiesel and its blends in stationary DI diesel engines. Only a few studies on use of biodiesel and its blends in automotive diesel engines or indirect injection diesel engines have been done. The effects of biodiesel and its blends on an automotive IDI diesel engine by comparison with local commercial diesel fuel<sup>28</sup> were studied in an experiment. *Jatropha curcas* methyl ester (JCME) and its blends had slightly lower torque, power output and thermal efficiency, but slightly higher BSFC than diesel fuel. In exhaust gas emission tests JCME and its blends significantly reduced HC, CO and Bosch Smoke Number but NOx emission slightly increased. The results indicated that B10 was the optimum fuel for the test engine.

A similar study carried out using both palm oil methyl ester (POME) and JCME with a DI engine yielded similar results.<sup>29</sup> Coconut (*Cocos nucifera*) is an edible oil, but because it is widely distributed all over Indonesia in areas where it is often difficult to provide fossil fuels which are consequently high in price, it
even becomes feasible to use coconut oil for fuel. Coconut methyl ester (CME) was field tested in vehicle and fishing boat engines as a fuel for use in remote areas.<sup>30</sup> In the vehicle road test, B30 CME was used as fuel for 15 000 km, and in fishing boat engine, B100 CME was used for 200 hours. Results indicated that as long as the biodiesel quality was according to Indonesian Biodiesel standard SNI 04-7182-2006, there were no significant differences in engine operation during the test by comparison with diesel.

Kapok nut (*Ceiba Pentandra* L.) is a non edible oil. Kapok trees are also widely distributed throughout Indonesia but not utilised as an energy source.<sup>31</sup> Biodiesel from Kapok seed oil was tested with a DI diesel using standard test procedures including engine injector nozzle coking test CEC F-23-A-01. Fuel consumption and smoke emissions increased. Nozzle tip deposits were very thick, presumably caused by the content of cyclopropenoid. Hydrogenation would be required to crack the cyclopropenoid structure before transesterification to solve this problem.

Mixed biodiesel.<sup>32</sup> There is considerable potential for ASEAN to produce and supply various biodiesel products to the rest of the world due to its natural resource base; however, the use of biodiesel still presents a number of problems which need to be resolved, especially the high price of raw materials and the quality of biodiesel fuels. In view of these limitations, seeking ways to combine various biodiesel raw materials (e.g. edible and non-edible oils) is one strategy that could be used to solve the problems: reducing the economic cost, utilising the availability of raw materials and improving the quality of biodiesel fuels particularly cetane number, oxidation stability and cold flow properties. In this study, four biodiesel fuels were mixed to create three biodiesel fuel mixtures in differing weight ratios as follows: (1) 70% Jatropha curcas oil methyl-ester (JME) with 30% palm oil methyl ester (PME), (2) 70% JME with 30% coconut oil methyl ester (CME), and (3) 75% soybean oil methyl ester (SME) with 25% PME. Three kinds of mixed biodiesel fuels in form of B10 and B100 together with conventional diesel fuel have been tested in a DI diesel engine. Via analysing process based on the in-cylinder pressure data and rate of heat release, the obtained results showed that biodiesel fuel mixtures had similar cetane number to diesel fuel; this is the main factor to explain why three biodiesel fuel mixtures were selected to simulate the current used fuel - diesel fuel. Moreover, all mixed biodiesel fuels were comparable with conventional diesel fuel in performance and combustion efficiency and exhaust gas emissions were reduced significantly (e.g. THC, CO and PM). Especially, the reduction of NOx is an interesting issue in this study; this reduction could be explained by the rate of heat release obtained and the use of antioxidant BHA.

# 23.4 Utilisation of biodiesel B5 based cat-fish fat in diesel engines

In Vietnam, the master project of biofuels production until 2015, a vision to 2025 has been approved by decision 177/2007/QĐ-TTg of the government.<sup>33</sup> According

to this decision, in 2010, biodiesel production will be 50 thousand tons/year; in 2015, biofuels production will be enough for 5 million ton gasohol E5 and biodiesel B5; and until 2025, ethanol and biodiesel production will be 1.8 million tons that meets 5% of the national fuel requirement.

In order to complete the biodiesel production process and to utilise biodiesel B5 (blend of 5% biodiesel and 95% market diesel) in engines, a national research project, code DTDL.2007G/19, has been set up and run by Vietnamese Institute of Industrial Chemistry. Institute of Transportation Engineering, Hanoi University of Technology, is one of the collaborative institutions. The project was aiming biodiesel based cat-fish fat production and application of B5 fuel in diesel engines.<sup>34</sup>

## 23.4.1 Properties of biodiesel based cat-fish fat

Properties of biodiesel B100 produced under industrial pilot scale at the Institute of Industrial Chemistry are given in Table 23.6. It is shown in this table that the

Properties	B100 limits	B100 produced TCVN7717-07	Test method
Methyl ester, wt.%	96.5 min	98.4	EN 14103
Density at 15°C, kg/m <sup>3</sup>	860–900	878.9	TCVN 6594 (ASTM D 1298)
Flash point, °C	130.0 min	150	TCVN 2693 (ASTM D 93)
Water and sediment, % vol	0.050 max	0.005	ASTM D 2709
Kinematic viscosity 40°C, mm²/s	1.9–6.0	4.6	TCVN 3171 (ASTM D 445)
Sulphated ash, wt.%	0.020 max	0.001	TCVN 2689 (ASTM D 874)
Sulphur, ppm	500 max	50	ASTM D 5453/TCVN 6701
Copper strip corrosion	N°1	1a	TCVN 2694 (ASTM D 130)
Cetane number	47 min	51	TCVN 7630 (ASTM D 613)
Cloud point, °C	Report	+10	ASTM D 2500
Carbon residue, 100% sample, wt.%	0.050 max	0.019	ASTM D 4530
Acid number, mg KOH/g	0.50 max	0.35	TCVN 6325 (ASTM D 664)
lodine value, g/100g	120 max	44.3	EN 14111/TCVN 6122
Oxidation stability at 110°C, hours	6 min	6.2	ASTM D 2274/EN 14112
Free glycerin, wt.%	0.020 max	0.018	ASTM D 6584
Total glycerin wt.%	0.240 max	0.184	ASTM D 6584
Phosphorus content, wt.%	0.001 max	0.0006	ASTM D 4951
90% distillation fraction temp, °C	360 max	337	ASTM D 1160
Sodium/potassium, combined, mg/kg	5.0 max	3	EN 14108, EN 14109

Table 23.6 Properties of produced biodiesel B100 in comparison with TCVN standard limits

Properties	B5	Proposed B5 limits
Density at 15°C, kg/m <sup>3</sup>	844.2	820-860
Flash point, °C	77	55 min
Water and sediment, % vol	0.007	0.02 max
Kinematic viscosity 40°C, mm <sup>2</sup> /s	3.91	2-4.5
Sulphated ash, wt.%	0.0025	0.01 max
Sulfur, ppm	470	500
Copper strip corrosion, 50°C, 3 hours	1a	1
Cetane number	54	46 min
Cloud point, °C	-3	6 max
Carbon residue, 100% sample, wt.%	0.0487	0.03
90% distillation fraction temp, °C	346	360 max

*Table 23.7* Properties of cat-fish fat based biodiesel blend B5 fuel and proposed Vietnamese standard limits for biodiesel B5

produced biodiesel B100 meets all requirements of Vietnam standard on Biodiesel B100 (TCVN7717-07).<sup>35</sup> The cloud point of 10°C of biodiesel B100 requires an additive to reduce for storage in biodiesel 'neat' form; however, within the pilot scale production, the fuel is stored in B5 form so this matter was not mentioned.

Following a specific blending procedure, biodiesel B5 blend (5% B100 and 95% market diesel) was produced. This biodiesel B5 meets almost all limits of the proposed Biodiesel B5 standard described in Table 23.7. In addition, due to low percentage of biodiesel B100 in the mixture, the B5 fuel has quite close properties with those of market diesel and standard limits of petrodiesel given in TCVN 5689-2005.<sup>36</sup> The cetane number, flash point and kinematic viscosity are in turn of 54, 79 and 3.91, slightly higher than those of market diesel (in turn of 51, 78 and 3.87). These properties of Biodiesel B5 analysed within the mentioned national research project have contributed remarkably for Directorate for Standards, Metrology and Quality to develop B5 fuel standard in Vietnam.

### 23.4.2 Experimental set up and apparatus

The DTDL.2007G/19 project includes many testing objects such as engines, passenger cars, light duty vehicles,<sup>34,37–39</sup> the findings from testing engines are presented in detail as follows.

The testing objects include 02 diesel engines D243, Belarus made. One used market diesel, another used biodiesel B5. These engines are usually used in tractors and fishing boats. Specifications of the testing engines are shown in Table 23.8.

Comparative tests were conducted on load curves and speed curves to investigate impacts of B5 fuel on engine's performance. To assess exhaust emissions, R49 driving cycles (equivalent to Euro 2 emission standard – the one currently applied for heavy duty vehicle engines in Vietnam) were used for the testing engines.

Specifications	
Engine modelDEngine typeInFuel supplying systemMNumber of cylindersForBore × stroke17Displacement4.Compression ratio16Power/rated speed80	243 -line, diesel, four stroke lechanical direct injection our 10 mm × 125 mm 749 litres 5.4:1 DHP/2200rpm

Table 23.8 Specifications of the testing engines

The two testing engines were also operated within 300 hours durability tests to assess engine components, lubrication oil, as well as engine's performance and exhaust emissions.

The test-cell used to conduct comparative tests and durability tests is high dynamic engine AVL test-cell for heavy duty vehicle's engines at Laboratory of Internal Combustion Engine, Institute of Transportation Engineering, Hanoi University of Technology.

Emission bench CEBII was used for gaseous emissions analysis. Particulate matter was sampled by the AVL Smart sampler 743. The testing apparatuses are presented in Fig. 23.19.



23.19 Installation of the testing engine in the test-cell.

### 23.4.3 Test results and discussion

#### Findings from performance tests

The engine power (P) and BSFC at full load of the same engine running with market diesel (Do) and biodiesel B5 (B5) are given in Fig. 23.20. It is observed in Fig. 23.20 that engine power is higher and BSFC is lower with B5 fuel at all measuring points, although the improvement is not much due to low percentage of biodiesel in the blend. The average engine power was increased 1.34% while averaged BSFC was reduced 1.29%. The detailed explanation of this effect will be shown together with impacts of B5 on exhaust emissions below.

Impacts of biodiesel B5 fuel on exhaust emissions in comparison with the market diesel can be observed in Fig. 23.21.

It is depicted in Fig. 23.21 that using B5 fuel the HC, CO and PM were reduced 12.29%, 8.60%, 2.25% respectively, while NOx was increased 1.93%. The reduction of HC, CO and PM, and the increasing of NOx emissions with biodiesel fuels have already been mentioned by many researches. Those shown in Fig. 23.22 by U.S. Environmental Protection Agency (EPA)<sup>40</sup> are an example of these effects.

Average emission changes found by the EPA for B20 (a blend of 20% biodiesel with conventional diesel) also showed significantly lower levels of emissions of specific toxic compounds for biodiesel and biodiesel blends, including aldehydes, PAH (polycyclic aromatic hydrocarbons), and nitrated-PAH.<sup>40</sup> However, a number of factors such as different fuel system designs, engine calibrations, fuel



*23.20* Comparison of engine power and brake specific fuel consumption as the same engine was run with market diesel and biodiesel B5 fuel.



*23.21* Comparison of exhaust emissions as the same engine was run with market diesel and biodiesel B5 fuel.



23.22 U.S. Environmental Protection Agency evaluation of biodiesel effects on pollutant emissions for heavy-duty engines.<sup>22</sup>

quality and blending rate can cause biodiesel emissions to differ significantly from the average values.

The increasing of NOx was shown to be related to a small shift in fuel injection timing caused by the different mechanical properties of biodiesel relative to conventional diesel. Because of the higher bulk modulus of compressibility (or speed of sound) of biodiesel, there is a more rapid transfer of the fuel pump pressure wave to the injector needle, resulting in earlier needle lift and producing a small advance in injection timing.<sup>41</sup>

Of the testing case, 5% of biodiesel in the blend did not affect much in the reduction of the energy content comparing with that of the market diesel, while the structural oxygen content of a biodiesel fuel improved its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than that of petrodiesel. The results were that, with the biodiesel B5 fuel, the engine power was increased, CO, HC and PM emissions were reduced. Because of low energy content of the biodiesel, higher biodiesel blends may lead to lower engine power and higher fuel consumption.

#### Findings from durability test

Variance of engine power and fuel consumption in percent (%) comparing with those parameters before 300 hours durability test of each testing engine is depicted in Fig. 23.23. Where D243-B5 and D243-Do are in turn of the testing engine fuelled with biodiesel B5 and market diesel; D243-B5-150h means the testing engine D243 fuelled with biodiesel B5 after 150 hours. The same definitions are applied for D243-B5-300h, D243-Do-150h and D243-Do-300h.

As shown in Fig. 23.23 the engine power decreased and the fuel consumption increased after 150 hours and 300 hours durability test. Although the differences are not much due to short period running time, there is a clear consensus in the changes of engine power and fuel consumption. The fact that the engine fuelled with biodiesel B5 had lower changes of engine power and fuel consumption after 150 hours and 300 hours durability test is not relevant with other research results which showed higher engine wear when the engine was fuelled with biodiesel.<sup>1</sup>

Exhaust emissions were measured before, after 150 hours and after 300 hours durability test following R49 driving cycle. Results are given in Fig. 23.24.

It is shown in Fig. 23.24 that none of the emission components meets Euro2 emission standard limits. This reveals somehow the current emission quality of the diesel engine in Vietnam. The emission components HC, CO and PM were risen but NOx depleted with the test period. These results match with the deflection of engine power and fuel consumption as mentioned above, again longer testing period is needed to have better evaluation of engine durability.

Principally, as the wear of engine's parts increased after a certain time of operation, compression pressure reduced and more combustion products blew to



*23.23* Deflection in percent of engine power and fuel consumption during 300 hours durability test.



*23.24* Deflection in percent of emission components during 300 hours durability test.

crankcase, the combustion process of the engine deteriorated causing worse engine's performance, high hydrocarbon, carbon monoxide and particulate matter were formed, whilst nitrogen oxide reduced due to lower temperature.

There was no damage observed to the engine's components during 300 hours durability test with biodiesel B5 fuel. The potential coking of the injector was not found as the kinematic viscosity of the biodiesel B5 fuel is almost equal to that of the market diesel. However, this has to be considered with higher biodiesel blends because high viscosity of the biodiesel causes larger fuel droplet sizes. The fuel droplet size is a function of surface tension, density and viscosity. Since the viscosity of biodiesel is high, the fuel droplets are large and hence may not be fully burned. The remaining biodiesel may then decompose at high temperatures (430–480°C) and form deposits.

# 23.5 The concept of using biofuel in engines (prime movers)

From many years experience researching the applications of alternative fuels, it is clear that the alternative fuels depend on the design requirements of the prime mover matching the characteristic properties of the fuel used and the characteristic properties of possible alternative fuels. When the designed fuel requirement of the prime mover is matched with the characteristic properties of an alternative fuel, the prime mover will operate as designed. But when the properties of an alternative fuel do not match, the prime mover will operate outside (*off design*) its designed operating conditions and naturally the output (performance: power, fuel consumption, efficiency, etc., emission: exhaust gas emission, noise, etc., life time) will also be affected.

There are two ways to solve this problem. Firstly the prime mover design requirement for fuel characteristics may be converted (adapted) to match the characteristic properties of the alternative fuel. Alternatively the characteristic properties of the alternative fuel may be converted (adapted) to match the designed fuel requirements of the prime mover. This concept is illustrated in Fig. 23.25. The most important requirement for the interface is that the standard must be met to satisfy requirements of both sides. Which choice to use and how far to convert each will depend on many factors, including location, technical, and economic, social and political aspects. For example in the case of biofuel for a high technology engine which has a design requirement for a high quality fuel, fuel conversion (adaptation) to a vegetable based oil may require transesterification to produce FAME to fulfil the high quality standard of fuel needed. But, for a stationary diesel engine where the operating condition is relatively constant, the required level of fuel quality may be relatively low, so a PPO with a lower production cost may be suitable. However, adapting the engine to use the PPO fuel may require the addition of a fuel heating system, a second fuel tank and a switching system to enable starting of the engine on diesel to warm up the engine and heat the PPO



23.25 The concept of using alternative fuel (AE) on prime mover (PM).

fuel and switch back to diesel before stopping the engine to flush the fuel system with diesel.

Clearly, when an engine designed for a certain fuel is converted to run on an alternative fuel, it is very important to see that the design need of the engine for the characteristic properties of the fuel is matched by the characteristic properties of the alternative fuel. Consequently it is very important to establish effective standards for alternative fuels.

## 23.6 Conclusions

As the majority of ASEAN countries are located in humid tropical regions, many different plant oils and animal fats are available as sources of biofuel feedstock. Consequently the properties and quality of differing biofuels vary considerably. The use of alternative fuels depends on matching the characteristic properties of the fuel for which the engine was originally designed with the characteristic properties of possible alternative fuels. When the design fuel requirement of the engine closely matches the characteristic properties of the alternative fuel, the engine will operate as designed, whereas if the properties of the alternative fuel do not match, the engine will operate outside (*off design*) the design operating conditions and performance will be affected.

To solve this problem the engine design requirement for fuel characteristics may be altered or adapted to match the characteristic properties of the alternative fuel or the characteristic properties of the alternative fuel may be adjusted or adapted to match the design fuel requirements of the engine. The requirements of both sides must be satisfied. What choices are made and how far adjustments are made in either respect, depends on many factors, including location, technical, and economic, social and political aspects.

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