Chapter 7
Liquid and Gaseous Biofuels for the Transport Sector

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Abstract In regards to a demand-oriented biofuel supply for the transport sector, this chapter considers the most relevant technologies and concepts for the production and supply of the most important liquid and gaseous biofuels and their current status quo. The limits of and opportunities presented by flexible biofuel production are considered. It has to be noted that flexible or part load operation of biofuel plants is not common. This also applies for most engineering plants in the chemical industry. Today biofuel plants are most commonly constructed as multiproduct plants such as bio refineries. Since the most inflexible step has an effect on the general system flexibility, intermediate storage, raw materials and various products are utilized in order to increase the system flexibility. Flexible management (i) of raw material and other input streams such as auxiliaries (reaction media, catalysts) and (ii) of plant operation in terms of main and by-products including the provision of products with high flexibility in application, is much more common than part load. In the article these opportunities are discussed for existing and new biofuel concepts. Furthermore, general issues of costing and environmental impact are considered.

7.1 Introduction

At present the transport sector accounts for half of global mineral oil consumption and nearly 20 % of world energy use. There will also be increased demand for transport fuels in the future. On a global level approx. 116 EJ a^{-1} are expected until 2050; i.e. an increase of about 25 % compared to 2009 (93 EJ a^{-1}) [13]. The total demand for biofuel is expected to account for 27 % of the total transport fuel demand in 2050 [12]. Biofuels are promoted as one of the best means to account for the predicted increase in future consumption in addition to targeting other priorities such as improved efficiency, traffic reduction and relocation, and electro mobility (Chap. 2). Large quantities may be in demand however due to the complex state of

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affairs in regards to the raw material base for biofuels, the uncertainty surrounding biofuels must be taken into consideration (Chap. 3).

In regards to a demand-oriented biofuel supply for the transport sector, this chapter considers the most relevant technologies and concepts for liquid and gaseous biofuels and their current status quo. Furthermore, the limits of and opportunities presented by flexible biofuel production are briefly discussed.

7.2 Technologies

There are various methods to produce liquid and gaseous fuels from biomass. The purpose of biomass conversion is to provide fuels with clearly defined fuel characteristics that meet given fuel quality standards. Depending on the method of biomass conversion there are three main pathways to consider; all of them are part of specific overall concepts that are characterized by different grades of technological complexity and flexibility [14, 20]:

Physico-chemical Conversion Such processes usually use low temperatures and pressure levels. They include the production and treatment of oil and fat containing biomasses into triglyceride biomass (e.g. vegetable and animal fats and oils) and fatty acids. These raw materials are processed further with alcohols through catalyzed trans-/esterification into biodiesel or fatty acid methyl ester (FAME). It is used in pure form in specially adapted vehicles or is blended with diesel.

Biochemical Conversion These processes involve using microorganisms to convert the biomass (usually sugar and starch fractions) into liquid and gaseous fuels. For instance bioethanol is produced by fermenting sugars from starch and sugar biomass. It is applied in pure form in specially adapted vehicles or blended with gasoline, provided that fuel specifications are met. Another method is using biogas resulting from the anaerobic treatment of biogas substrates, which is then upgraded to biomethane and can then be fed into the natural gas grid and e.g. used in natural gas vehicles. Both of these current developments involve the application of special treatment processes (hydrolysis via thermal processes or enzymes) that succeed in breaking down lignocellulosic biomasses and releasing sugars, which can then be fermented into alcohol or digested.

Thermo-chemical Conversion These processes use high temperatures and pressure levels to turn biomass (usually lignocellulosic fractions) via different methods such as torrefaction, pyrolysis or hydrothermal processes into different products (i.e. depending on process conditions usually into solid, liquid and gaseous fractions) that can be either upgraded or further processed, e.g. via gasification (see also Chap. 8). Gasification based process chains include conversion into a raw gas that is then treated and conditioned into a synthetic gas consisting mainly of carbon monoxide and hydrogen. This gas can be processed further into different types of liquid and gaseous fuels via different fuel synthesis and upgrading technologies. Fuels

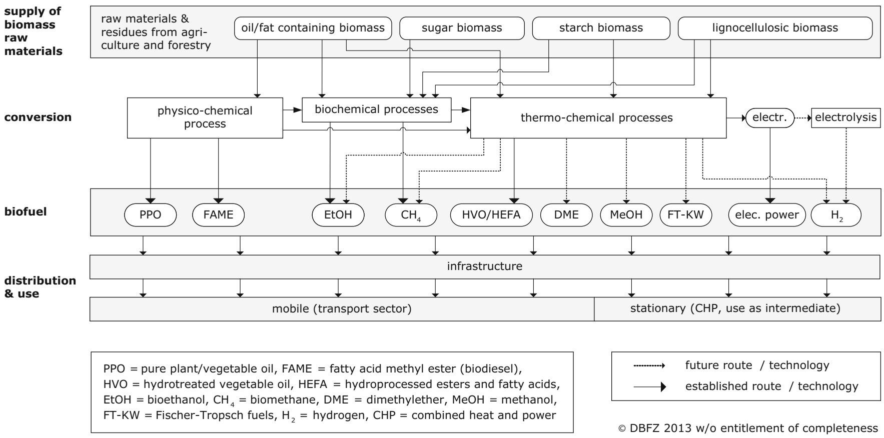

Fig. 7.1 Overview of biofuel options (Adapted from [21])

from this route are then called 'synthetic biofuels'. The most promising liquid synfuel (also BTL, biomass-to-liquids) is e.g. Fischer-Tropsch (FT) fuels due to its favourable fuel properties. Furthermore, alcohols (e.g. ethanol and methanol) can also be produced. Gaseous synfuels are e.g. dimethylether (DME) and biobased synthetic natural gas (Bio-SNG), which is also a form of biomethane and can be similarly used as a natural gas substitute such as biomethane from biogas. Furthermore, available vegetable oils or animal fats from physical-chemical conversion can be treated by hydrotreating processes into so called hydrotreated vegetable oils or esters and fatty acids (HVO/HEFA), a biodiesel with comparably more favourable properties than conventional biodiesel.

A comprehensive overview of the overall supply chains of the most important biofuel options under international discussion is provided in Fig. 7.1.

7.3 Concepts and State of the Art

Usually, within a certain biofuel route (e.g., bioethanol) overall concepts for biofuel production plants are quite different; they cannot be bought off the shelf. In regards to those already in existence, the concepts which have been realised are dependent on the specific local conditions and infrastructure, the equipment provider and certain optimisations through the biofuel production plant operator itself. Each biofuel concept must therefore be considered individually.

Today, biofuel production plants most commonly exist as so called multiproduct plants such as biorefineries. According to [9], material and energy-driven biorefineries can be distinguished. Much of the existing network of biorefineries already has a strong link to biofuel production or energy-driven biorefineries [16]; for instance by-products that are available in addition to the main product biofuel such as fodder, fertiliser, products for further processing in feed, cosmetic and chemical industry. Furthermore, some of the biofuels can also be used in the intermediary stage before further processing in different industry branches (e.g., bioethanol, biomethane, biodydrogen, Fig. 7.1).

According to this, a selection of current and future biofuel options are considered; a summary of their typical technical characteristics, status quo as well as international production rates and capacities is given in Table 7.1.

In addition to the given biofuel capacities in Table 7.1, the development of biofuel production capacities is provided in Fig. 7.2. While biodiesel capacities (mainly based on rape) decreased caused by the development of a policy frame and thus market conditions, bioethanol (based on wheat, rye and sugar beet) slightly increased. In comparison, biomethane (based on different energy crops but also stillage from bioethanol production) capacities showed significant growth in the past years, despite the use of biomethane in different sectors.

7.4 Options for Flexible Production of Liquid and Gaseous Biofuels

Regarding the general options for flexible operation in terms of demand-oriented biofuel supply, biofuel production plants are not comparable to those used for electricity and/or heat/cooling. They can usually be compared with conventional chemical process engineering facilities. Such facilities are usually either running on nominal load mode or not; the part load mode typically used for power production by applications such as combined heat and power engines are not usual for plants producing biofuel. This is due to the fact that products like biofuels can usually be stored much easier than e.g. electricity. The reasons for this so called static operation include relatively easy operation and controlling. Furthermore, most of the facility units are most efficient when operated at their designed nominal load.

Since the most inflexible step has an effect on the general system flexibility, intermediate storage, raw materials and various products are utilized in order to increase the system flexibility. In terms of biofuels the possible ways to achieve flexible plant operation concentrate on the following key objectives:

- Flexible management of raw material input or other input streams such as auxiliaries (reaction media, catalysts),
- Flexibility management of plant operation in terms of main and by-products, including provision of products with high flexibility in application.

The mentioned objectives are mainly driven by the respective market situation which is dependent on external disturbances like fluctuations in the resource and product markets (e.g., volatile and dynamic price developments), policy framework and certain subsidies.

Some exemplary approaches for existing and new concepts will be discussed at a later point.

Table 7.1 Typical technical characteristics and status quo of selected biofuel options

Characteristics	Liquid biofuels					Gaseous biofuels		
	Biodiesel (FAME)	Hydrotreated vegetable oils or esters and fatty acids (HVO/HEFA)	Bioethanol		Synthetic biomass-to-liquids (BTL)	Biomethane/ Biogas	Biomethane/ Synthetic Natural Gas (SNG)	Biohydrogen
Raw materials	Vegetable and animal oils and fats (e.g. rape, soya, palm, grease/used cooking oils, algae oils)	cf. biodiesel	Sugar (beets, cane), starch (corn, wheat, rye)	Lignocelluloses (straw, bagasse, wood, switch grass)	Lignocelluloses (diverse, focus wood, straw, residues such as black liquor)	Sugar and starch, organic residues (e.g. biowaste, manure, stillage)	Lignocelluloses (diverse, focus wood, straw)	Lignocelluloses (diverse, focus wood, straw)
Main conversion steps/plant concept	Vegetable oil production (mechanical or solvent extraction), refining, trans-/esterification, biodiesel treatment	Vegetable oil production (mechanical or solvent extraction), refining, hydrotreating, destillation	Treatment, sugar extraction or hydrolysis/saccharification, C6 fermentation, distillation, final dehydration	Pretreatment (thermal, acid etc.), hydrolysis, saccharification, C6/C5 fermentation, distillation, final dehydration	Mechanical and thermal treatment (e.g. drying, pyrolysis, hydrothermal), gasification, gas treatment, synthesis (e.g. Fischer Tropsch, FT), hydrocracking, distillation, isomerisation	Silaging, hydrolysis (optional), anaerobic digestion, gas treatment and upgrading	Mechanical and thermal treatment (e.g. drying), gasification, gas treatment, synthesis (methanation), gas upgrading	Mechanical and thermal treatment (e.g. drying), gasification, gas cleaning, reforming, gas upgrading

(continued)

Table 7.1 (continued)

Characteristics	Liquid biofuels					Gaseous biofuels		
	Biodiesel (FAME)	Hydrotreated vegetable oils or esters and fatty acids (HVO/HEFA)	Bioethanol		Synthetic biomass-to-liquids (BTL)	Biomethane/ Biogas	Biomethane/ Synthetic Natural Gas (SNG)	Biohydrogen
By-products[a]	Press extraction, glycerine, salt/ fertiliser, fatty acids, other oleochemicals	(Press extraction), propane, gasoline fractions	Sugar: bagasse/ vinasse/starch: gluten, stillage for DDGS (Distiller's Dried Grains with Solubles), fertiliser, biogas/ biomethane, technical CO_2	Lignin or lignin based by-products, pentoses, stillage products such as fertiliser, biogas/ biomethane, technical CO_2	In case of FT, waxes, naphtha, electricity and heat	Digestate (e.g. as fertiliser), electricity	Electricity and heat	Electricity and heat
Status of technical development	Commercial	Commercial	Commercial	Demonstration	Pilot for FT fuels	Commercial	Demonstration	Pilot
Plant capacity[b]	2–350 MW	255–265 MW (150–1,220 MW)	38–450 MW	0.5–5 MW (35–100 MW)	0.8–5 MW (40–300 MW)	0.5–50 MW	1–10 MW (20–200 MW)	0.5–10 MW (5–100 MW)
Efficiency[c]	38–92 %	58–90 %	30–85 %	37–77 %	49–60 %	53–76 %	62–74 %	47–78 %

<table>
<tr><td>Installed capacity | production worldwide[d]</td><td>50 mn t a^{-1} | 17 mn t a^{-1}</td><td>2.2 mn t a^{-1} | unknown</td><td>90 mn t a^{-1} | 70 mn t a^{-1}</td><td>0.108 mn t a^{-1} | unknown, often only test campaigns</td><td>0.033 mn t/a | unknown, often only test campaigns</td><td>1.21 mn t a^{-1} | unknown</td><td>Not used outside Europe</td><td>Unknown</td></tr>
<tr><td>Installed capacity | production EU[d]</td><td>22 mn t a^{-1} | 8.8 mn t a^{-1}</td><td>1.2 mn t a^{-1} | 840 mn t a^{-1}</td><td>5.8 mn t a^{-1} | 5.2 mn t a^{-1}</td><td>0.019 mn t a^{-1} | unknown, often only test campaigns</td><td>No plants in operation</td><td>0.71 mn t a^{-1} | 0.69 mn t a^{-1}</td><td>0.092 mn t a^{-1} | unknown often only test campaigns</td><td>Unknown</td></tr>
<tr><td>Installed capacity | production Germany[e]</td><td>4.5 mn t a^{-1} | 2,4 mn t a^{-1}</td><td>No plants in operation</td><td>0.9 mn t a^{-1} | 0.6 mn t a^{-1}</td><td>0.001 mn t a^{-1} | unknown, only test campaigns</td><td>No plants in operation</td><td>0.45 mn t a^{-1}| 0.39 mn t a^{-1}</td><td>No plants in operation</td><td>No plants realised</td></tr>
<tr><td>Link to biorefinery platforms[f]</td><td>Oilseed or vegetable oil biorefinery</td><td>Oilseed or vegetable oil biorefinery</td><td>Sugar and starch biorefinery</td><td>Lignocellulosic biorefinery</td><td>Lignocellulosic or synthesis gas biorefinery</td><td>Biogas biorefinery</td><td>Lignocellulosic or synthesis gas biorefinery</td><td>Lignocellulosic or synthesis gas biorefinery</td></tr>
</table>

[a]Usually depending on process design

[b]Related to biofuel output – w/o brackets for current capacities, expected capacities in future in brackets

[c]Overall energetic efficiency according to [18] (ratio of output energy flow of main and all by-products incl. excess process energy to input energy flow of raw material, auxiliaries, external process energy)

[d]Values for 2011 or 2012 based on [1, 22]

[e]Values for 2012 based on [5]

[f]According to Joint European Biorefinery Vision for 2030 [16] and/or the German Biorefineries Roadmap [9]

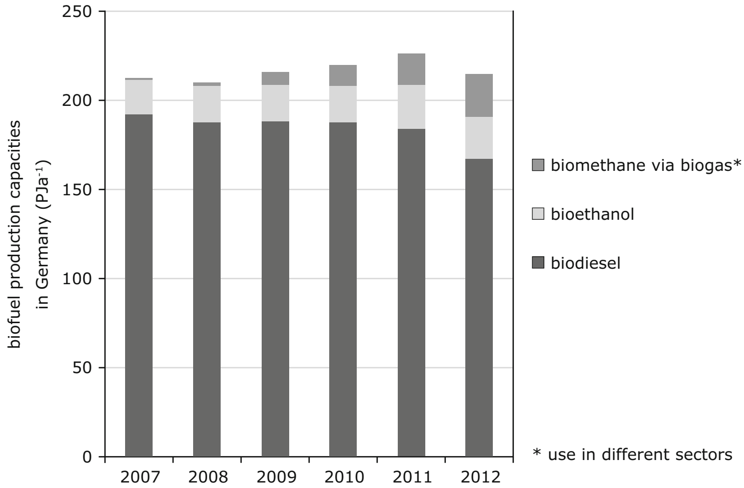

Fig. 7.2 Development of biofuel production capacities in Germany (Adapted from [21])

7.4.1 Approaches for Existing Concepts

As mentioned above existing, biofuel concepts are usually conceived for static operation. Due to the possible storage methods (over a certain period) of the different raw materials, namely liquid fuels in tanks and gaseous fuels like biomethane via the natural gas grid, they are usually running on nominal load and have to deal with production downtimes in case of e.g. volatile market prices of raw materials and product sales challenges. Published information on operation modes is scarce. For biochemical fermentation processes such as for bioethanol and biogas, changes in fermentation can take up to several days, whereas modifications in the running of process engineering plants can take minutes to hours. Examples for biodiesel and bioethanol are given in the following. Flexibility of biomethane from upgraded biogas is discussed in Sect. 8.4.2.

Example Biodiesel Despite the biodiesel production technology (continuous, batch or semi-batch as well as single or multi-feedstock) usually plants run batchwise on different raw materials (Table 7.1). On the background of the current policy frame in Europe/Germany (which is doubly important for biofuels based on residues for the biofuel quota) plant operators, producing biodiesel based on multi-feedstock technologies and using cooking oil and animal fats, have, for instance, announced an increase of the plant utilization rate of approx. 53–81 % in recent years. This increase is a result of a change in raw material with little production downtime [23]. This does not apply for biodiesel plant operators who use vegetable oils (Table 7.1); in these cases, the rate of plant use decreases from more than 80 % to less than 40 %. The installed overcapacity of biodiesel plants especially in Europe is another reason for this occurrence [12].

Example Bioethanol In regards to flexible plant management, a prominent example is bioethanol production in Brazil. Traditionally, bioethanol is accrued as a by-product of sugar production as the sucrose content of the sugar cane is used in an optimised approach [10]. A number of factors influence the economics of bioethanol production in Brazil, including (i) the development of world prices for sugar, (ii) harvesting results and the quality of sugar cane production, (iii) government-controlled domestic prices for gasoline, (iv) tax policies and (v) exchange rate of Brazilian currency. As Brazil and India are the world's largest producers of sugar they have a major impact on sugar prices. This effects Brazils facility operators in determining how much of its sugar cane production should be refined as sugar or processed to bioethanol [10, 24].

A similar situation occurred in 2007, when a German bioethanol plant operator, who was only producing bioethanol, shut down his plant and sold his contracted raw material, cereal, to the market, which was more profitable than producing bioethanol.

The influence of production plant design (e.g., often efficiency-driven approach) can be illustrated for example by the collapse of the largest corn ethanol biofuel company in the US during the period of high raw material prices around 2007/2008. This operator was using more efficient dry-mill technology (i.e. higher ethanol yield per corn input and lower capital investments). However, due to the limited flexibility of the raw material in question (here just corn grain) and the production of just one primary product (bioethanol), a fair profit margin could not be maintained because of fluctuating market conditions. In comparison, a traditional less efficient wet-mill plant (i.e. lower ethanol yield per corn input and higher capital investments) has a more diverse and adjustable product portfolio (e.g., corn syrup, starch, and ethanol) and thus a better chance of survival in volatile markets [2].

7.4.2 Approaches for New Concepts

While existing biofuel plant concepts are not that flexible it is suggested that in future biofuel and/or biorefinery concepts, operational flexibility needs to be a key issue in order to increase long term economic performance and in effect increase chances of survival when faced with external disturbance [15]. So called flexible polyproduct or polygeneration plants try to produce the most profitable products by altering production according to market fluctuations and thus have the potential to achieve better economic performance compared to conventional static plant operation. However, such flexibility alters the production rate of certain products by oversizing equipment and thus higher capital investments. One of the major challenges therefore is to design polyproduct concepts which take into account the optimal trade-off between operational flexibility and capital cost [2]. Moreover, also plant size of such biorefineries is of major importance with regard to raw material availability and logistic requirements. Especially compared to conventional fossil fuel based refineries or chemical plant they range in the small to medium size.

Example Lignocellulosic Bioethanol The known concepts, which are still in the pilot or demonstration phase for the production of bioethanol based on lignocellulosic biomass (Table 7.1), focus primarily on the production of bioethanol as biofuel [1]. Despite this primary focus, biorefinery concepts also consider the production of bioethanol and other products such as ethylene or carbon acids (e.g. Bioeconomy cluster Leuna in Germany [6]).

Example Biomethane via Bio-SNG Despite the fact that biomethane can be stored for a long period of time in storage facilities in the natural gas grid (see Sect. 8.4.2), the gasifier employed in the process chain is of very limited flexibility (increasing in the order fluidised bed and entrained flow gasifier) and thus also the flexibility of the applied biomass raw material. Catalytic synthesis plants are at present rarely operated in part load mode. However, increasing flexibility in this case is an important research topic. The deployment time of methanation synthesis is approx. 5 min, the cold start a matter of hours, the energy requirement for standby is about 1 % of max capacity [7, 11].

Example BTL/Fischer-Tropsch Fuels In general, the Fischer-Tropsch (FT) process has two important weaknesses: (i) a low overall efficiency and (ii) the production of a wide range of different aliphatic hydrocarbons which makes intensive product separation and treatment necessary for the production of applicable fuels. There are many factors involved when considering the flexibility of the FT process. The produced liquid biofuel can be stored for a long, even indefinite period of time. Different storage technologies such as tanks or storage caverns are well-known for the storage of crude oil and refinery products.

When considering conversion technologies one drawback of FT synthesis as a part of polyproduct refineries is evident: a fixed production rate must be achieved because of the rigorous operational requirements of the gasifier. Thus the overall concept cannot easily be adapted to fluctuating demands [2]. This is described in detail in Chap. 8.

The third aspect is the flexibility of synthesis. Operating the reactor in partial load mode can influence the composition of the aliphatic hydrocarbon mixture because of the changing resistance time. Another important condition is a constant and homogeny temperature profile; this is the second important limiting factor. It is common to operate a plant in full load mode or to stop production completely for an extended period of time. Partial load operation of Fischer-Tropsch synthesis plants is much more complicated than of Bio-SNG plants and is difficult to realize.

One approach that has been investigated is the flexible integrated gasification polygeneration concept, which involves the use of different raw materials (e.g., coal and biomass) and the coproduction of hydrogen, FT fuels as well as methanol, urea and electricity. This approach aims at producing electricity during peak hours while switching to chemicals and fuels during off-peak hours. A high degree of flexibility can be achieved by limiting the operational load of 40–100 % in order to avoid problems in operation. While a complete switch from chemical to electricity production is possible for methanol and urea, for FT fuels the load is restricted to minimum of 60 % in order to avoid a gas turbine load of below 40 % [17].

Example Hydrogen Integration As a lot of the new concepts such as biomethane via Bio-SNG and BTL/Fischer-Tropsch fuels are based on synthesis, applying synthesis gas in addition to the limited flexibility of gasifier for the production of synthesis gas the use of renewable but not biogenous hydrogen is also an option to increase flexibility. Concepts involving the production of additional hydrogen through excess electricity are discussed [8, 7]. The concept behind this follows the ongoing debate surrounding the implementation of intermittent energy sources (IES, e.g. from wind and solar power production) in the existing energy system via so called power-to-gas (PTG) or power-to-liquid (PTL) applications. After this stage, excess electricity from the IES is used for hydrogen electrolysis [11]. In addition to other applications (e.g. accommodation to gas grid, direct use in different industries or for mobility or storage), this hydrogen can be implemented into syntheses like methanation or Fischer-Tropsch (Table 7.1) in order to increase the overall efficiency and economic viability of such SNG or BTL concepts. The addition of hydrogen from electrolysis is one way of adjusting the hydrogen to carbon monoxide ratio. The electrolysis can replace or supplement CO-shift. Furthermore, synthesis through the combined application of hydrogen from electrolysis and carbon monoxide is also possible. However, this is not a biomass application in the narrow sense.

7.5 General Economic and Environmental Aspects

For the efficient realization of these considered concepts, costs and selected environmental aspects are crucial. However, in spite of the fact that several investigations for static process operation have been published, information on flexible biofuel production plant operation is scarce. For this reason only a general overview follows in the section.

Costs Evaluating different cost alternatives is done to identify relative advantages, to compare different options and to determine important influencing factors. Local conditions are relevant in this evaluation. Sensitivity analyses for different biofuels show that in addition to annual full-load hours of the biofuel production plant, raw material costs and total capital investments are of great importance [20]. Furthermore, it should be noted that often market values for raw materials and by-products correlate with each other (e.g., oil seeds and press extraction, starch raw materials and DDGS, Table 7.1) [18]. For example, existing biodiesel production operations have been established with low TCI due to their comparably simple technical complexity. As a result, the impact of annual full-load hours per year is lower. However, the impact of raw material costs is crucial. This is in spite of the fact that there is an increasing tendency to increase total capital investments for biomethane and biofuels based on lignocelluloses in comparison to conventional biofuels. This is often due to more complex technologies and plant designs. However, for future biofuel concepts such as bioethanol, SNG or Fischer-Tropsch fuels, it can be assumed that with regard to biofuel production costs, considerable cost reductions are possible if proposed technical developments are realized [19].

Greenhouse Gas Emissions In regards to the existing frame conditions (e.g., Renewable Energy Directive 2009/28/EC [3] and Fuel Quality Directive 2009/30/EC [4] in Europe), the greenhouse gas mitigation potential of biofuels compared to fossil fuels has become an important value for biofuel marketing and sales. Greenhouse gas emissions are usually determined via life cycle analysis (LCA) which are carried out under different assumptions making it very difficult to compare the results from different studies. For instance, the GHG mitigation potentials for palm oil based biodiesel can range between 36 % and 71 % or 33 % and 66 % when rapeseed is used. The most important drivers for greenhouse gas emissions are (i) biomass production and (ii) biomass conversion to biofuel, including the overall efficiency of the designed concept [18]. These drivers are also important for the achievement of more flexible plant operation.

7.6 Conclusion

Through the consideration of a demand-orientated supply of biofuel for the transport sector, whilst also taking into account the most relevant technologies and concepts for the production and supply of the most important liquid and gaseous biofuels and their current status, the following can be concluded:

- Biofuel concepts are usually unique. They are dependent on the specific local conditions and infrastructure, the equipment provider and often the level of optimization, which is determined by the biofuel production plant operator.
- Flexible part load operation of biofuel plants is not common in comparison to most other process engineering plants in the chemical industry. Flexible operation for fuel synthesis processes is currently a research topic and is not ready for implementation. Today, biofuel plants are usually established as multiproduct plants such as biorefineries. Intermediate storage, raw materials or various products can also be used to increase system flexibility of such biofuel systems, especially when taking into account that the most inflexible step affects the system flexibility.
- Flexible management (i) of raw material and other input streams like auxiliaries (reaction media, catalysts) and (ii) of plant operation in terms of main and by-products, including the provision of products with high flexibility in application, is much more common than part load operation.
- Future flexible polyproduct or polygeneration plants will try to produce the most profitable products altering production according to market fluctuations. These plants will also have to face the major challenges of designing polyproduct concepts, which take into account the optimal trade-off between operational flexibility and capital cost.
- There are almost no investigations of flexible plant operation which consider costs and environmental issues. However, the most important drivers are raw materials (supply costs and emissions related to their production and supply) as well as conversion to biofuels (plant efficiency and annual load).

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