REVIEW OF BIOFUEL PRODUCTION – FEEDSTOCK, PROCESSES AND MARKETS

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ABSTRACT

Transportation fuels derived from biomass are an alternative to fossil-based fuels. Due to the fact that globally the available biomass resources are limited and considering the fact that they are also used as food materials there is an increasingly stronger need to use such organic matter as efficiently as possible (i.e. biorefinery approach). Against this background the overall goal of this article is to discuss the overall available biomass on a global scale. The article will also touch on the technologies to efficiently convert this biomass into transportation biofuels usable within the existing markets for such fuels and are presented in detail according to the current state of technology. Based on this, the global market for biofuels is discussed against the background of the available biomass resources. Finally the most important findings are summarised and presented.

Keywords: bioenergy, biofuels, biomass, technology readiness level.

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INTRODUCTION

Recent projections suggest that the global population as well as standards of living for most of the people will increase rapidly in the years to come (Department of Economic and Social Affairs, 2004). If this happens the global fuel demand is most likely to rise accordingly or even disproportionate due to increasing welfare and an increasingly mobile society (ExxonMobil, 2016). Considering that fossil fuels predominantly used on a global scale are limited resources characterised by very strong price fluctuations and their use exerting significant impact on the local/regional environment as well as the global climate, the question about the possible future role of biofuels within our global economy respectively, our global society is still not answered yet.

So far, biofuels contribute to a minor extent within the global mobility sector. Their share within a specific region is defined typically by policy driven measures (e.g. subsidies, tax exemption) implemented by several countries/groups of countries. Based on such administrative control tools a whole bundle of goals should be reached.

- Security of energy supply. The globally available and easily accessible crude oil resources are located mainly within a geographically clearly defined region characterised by severe political uncertainties (e.g. Arabian Spring, civil war in various countries, dictatorships, unstable monarchies). Thus, the security of energy supply has been and still is a strong driver for biofuels because so far they are produced from locally available domestic biomass as well as from biomass imported from a broad variety of countries (Timilsina, 2013; Månsson et al., 2014; Kisel et al., 2016).

- Sustainable energy provision. Globally society is pushing on very different levels towards continuously improving sustainability standards. This trend pushes on the one hand the use of renewables in general even in times of low oil prices. On the other hand, this development...
might limit the increased market introduction of biofuels because yields of primary production from agricultural and forestry might be affected by strengthened sustainability standards especially within the agricultural crop production (Linares and Pérez-Arriaga, 2013; Awudu and Zhang, 2012).

- **Greenhouse gas (GHG) reduction.** According to the Intergovernmental Panel on Climate Change (IPCC), it is necessary (with regard to climate change concerns) to keep the CO$_2$-eq concentrations within the global atmosphere in the 21st century at about 450 ppm or lower and thus to avoid an increase of the global temperature level of more than 2°C; in consequence this goal means a reduction of about 50% of global GHG emissions by 2050 and in fact a reduction of more than 80% in OECD countries (IPCC, 2015). Thus at national level in many nations/regions of the world specific reduction targets for GHG are addressed for: (i) the country as a whole and/or (ii) individual sectors of the economy. A reduction of GHG emissions can be accomplished within the transportation sector by shifts in both supply and demand structures e.g. (i) switch to low-carbon fuels (i.e. biofuels), (ii) efficiency improvements of engines, vehicles and additional appliances, (iii) modal shift (e.g. a shift in the transportation system, higher occupancy rates), iv) advanced freight logistics. Thus, GHG reduction has been and still is a strong driver for biofuels (Buchspies and Kaltschmitt, 2016; Wulf et al., 2017).

- **Job creation.** The creation of jobs in general and ‘green’ jobs in particular is on the global political agenda with a very high priority; this is especially true for countries with a comparable high unemployment rate. Additionally green growth and job creation have become an important part of the on-going development towards a more sustainable society. The use of biofuels could be one component within such a development.

- **Increased acceptance.** The pros and cons of biofuels are very controversially discussed within our society throughout the last decades. Thus, this on-going societal discussion process might support an increased use of biofuels in some cases and in other cases the opposite could occur. Nevertheless, due to the fact that this topic is discussed very emotionally severe consequences influencing the further development of the biofuel markets are most likely. As a result, the biomass resources used for biofuel production – and thus also the respective provision chain – might become more drivers in the years to come.

- **Food vs. fuel debate.** Also the food vs. fuel debate is still on-going on a global scale. This debate currently pushes new developments within the biofuel market in direction of the use of organic wastes as well as lignocellulosic biomass and agricultural crops not usable within the food and fodder market. On the opposite to this, for food security reasons, always and necessarily an over production of agricultural commodities is needed on a global scale and therefore the energy market could be a huge sink for the surplus production due to an easy substitution of fossil fuels by biofuels (Kline et al., 2016).

To sum up on the one hand side, there are strong drivers pushing for biofuels. On the other side, there are also considerable developments and trends hindering an increased use of such fuels based on organic matter. So far, no clear tendency can be identified either in Europe or globally; thus the use of biofuels has been more or less stable in recent years. Against this background the overall goal of this article is to assess possible options for biofuel provision related to the available biomass feedstock, the possible conversion processes and the expected markets. Thus, firstly, the available biomass resources are discussed below. Secondly, details concerning individual biofuel provision pathways are presented; this includes mainly fatty acid methyl ester (FAME), hydro-processed esters and fatty acids (HEFA), alcohol to long-chain hydrocarbons like e.g. alcohol-to-jet (AtJ), biogas-to-liquid (Bio-GtL), biomass-to-liquid (BtL) and hydro-treated depolymerised cellulosic jet (HDCJ). Afterwards these processes are compared to each other by different process related criteria. Thirdly, the markets for products coming from these various options are assessed based on the current situation. In the end, some final considerations concerning the future development and use of biofuels are given.

**RESOURCES FOR BIOFUEL PRODUCTION**

Biofuels can be derived from multiple biomass sources including by-products from forestry (e.g. forest and wood processing residues, short rotation forests), agriculture (e.g. crop residues, especially grown energy crops, animal wastes), and municipal waste (e.g. municipal solid waste excluding plastics and non-organic components, garden residues) as well as industrial waste (e.g. food processing wastes, scrap wood). Depending on climate, agricultural and forestry practices, accessible technologies, as well as the availability of land and its quality, the local/regional population density, the degree of industrialisation and the available waste management systems, the significance and availability of these various biomass sources varies substantially on a global level (Sims, 2007).
The processes to convert biomass into biofuels can roughly be categorised by the type of biomass used. Therefore, the biomass considered here is divided into biomass from forestry (i.e. mainly wood and industrial waste wood), biomass from agriculture (i.e. crops containing sugar, starch or oil as well as agricultural residues like straw) and organic waste streams (i.e. wet and dry organic waste products).

All over, the estimated global biomass potential for the period between 2010 and 2020 is around 160 EJ (exajoule) yr\(^{-1}\) excluding energy crops. If energy crops are taken into consideration, the total potential sums up to 245 to 363 EJ yr\(^{-1}\) (ensuring food security) according to the used energy crops. And the estimated global biomass utilisation varies from 75 to 77 EJ yr\(^{-1}\) in 2014 (Kaltschmitt et al., 2016).

**Biomass from Forestry**

Different types of biomass from forestry can be used for the production of biofuels; this biomass can be provided in different ways respectively can be retrieved from various steps within the overall provision chain for wood within our highly industrialised society.

According to Figure 1, forestry provides a significant amount of organic material on a global scale. For example, 2565 million tonnes (2013) of roundwood have been harvested without taken informal markets into consideration (i.e. local markets where wood is removed by the final user directly from the forest are not included into global market statistics) (Faostat, 2015). Roughly around one-third of this globally produced roundwood has been used as fuel wood. Assessed with the lower heating value this represents an energy potential of approximately 51 EJ yr\(^{-1}\). Under certain conditions a share of this wood mass might be available as a feedstock for biofuel provision.

In addition to the increasing amount of harvested roundwood, Figure 2 gives an overview of the development of the global forest area as an indicator of the amount of wood to be expected. This area has declined from approximately 4130 million hectares in 1990 to 4000 million hectares in 2013. This represents a global deforestation of approximately 3%, which again may vary extremely in different regions of the world. Whereas the cumulated forest area are in Africa and America showed the highest rate of deforestation (11% and 5%, respectively) the European forest area stayed mainly constant and the Asian forest area has even increased by approximately 7% (Faostat, 2015). By interpreting these values one has to keep in mind that the data base is partly poor for some countries. This might lead to a misinterpretation of these figures.

Another wood source could be energy wood from short rotation forestry (SRF). Willow and poplar which can be used for SRF show average yields of 10 t ha\(^{-1}\) yr\(^{-1}\) on a dry matter basis. In contrast, the amount of forest residues which can be utilised for energy purpose is usually estimated around 1 t ha\(^{-1}\) yr\(^{-1}\) on a dry matter basis (Kaltschmitt et al., 2016). In addition, the overall available biomass from forestry could be improved by an additional logging of e.g. low value wood components if this is possible on the background of a sustainable forestry management.

Another possible feedstock is industrial waste wood, which for example can be available in form of saw dust, offcuts or bark (Department of Environment, Food and Rural Affairs, 2008). The amount of industrial waste wood which could be used for biofuel production is hard to predict, since most of these industrial waste wood streams are used already energetically within the energy sector and/or as a raw material in the wood processing industry for e.g. particle board production (Merrild and Christensen, 2009).

Beside this, woody biomass can be used as a feedstock for biofuel provision after the use as a raw material (i.e. after the life time of the provided wood product has been expired). This is true for example
for demolition wood and/or for wood waste from residential areas (e.g. old furniture). Wood from demolished houses adds up to this.

**Biomass from Agriculture**

Biomass from agriculture can be subdivided related to different types of agricultural crops as well as the various components of plants. This includes e.g. energy crops containing sugar, starch or oil as well as agricultural residues like straw. Thus, the overall plant (i.e. the lignocelluloses) as well as certain parts of the plant (e.g. oil from oil containing plants (e.g. oil palms, rape, soya), sugar from plants containing sugar (e.g. sugar cane or sugar beet) or starch (e.g. wheat, corn) can be used for biofuel production (Sims et al., 2006).

To show possible yields, e.g. in Brazil with average sugar cane yields of approximately 80 t ha⁻¹ yr⁻¹ about 11 t ha⁻¹ yr⁻¹ of sugar can be harvested (Somerville et al., 2010). In Germany with an average wheat yield of 8 t ha⁻¹ yr⁻¹ approximately 1.3 t ha⁻¹ yr⁻¹ of sugar can be produced via starch liquefaction and saccharification. Additionally, straw can be used in theory. Exemplarily under German conditions wheat straw shows typical yields of 8.6 t ha⁻¹ yr⁻¹ on a dry matter basis. Approximately 75% of this organic matter consists of cellulose and hemicellulose. With an acidic pre-treatment and a subsequent enzymatic hydrolysis 76% of the cellulose and hemicellulose can be converted into sugar in theory; thus sugar yields of 4.9 t ha⁻¹ yr⁻¹ are possible (Saha et al., 2005).

Also the oil yield varies significantly due to regionally different cultivation conditions as well as varying types of seeds grown locally. For example, typical oil plants such as oil palms, soya plants or rape plants are characterised by oil yields between 0.5 and 5.5 t ha⁻¹ yr⁻¹ (Zimmer, 2010). At present, the use of non-food vegetable oil (for instance derived from *Jatropha curcas* L.) for biofuel production is politically driven in comparison to other feedstocks. *Jatropha curcas* L., if cultivated under optimal conditions, can achieve seed yields of about 4 t ha⁻¹ yr⁻¹ (Wahl et al., 2012) with an oil content of about 35% (van Eijck et al., 2010). Based on this an average oil yield of 1.1 t ha⁻¹ yr⁻¹ can be achieved (pressing and pre-treatment losses of approximately 25%) for small scale rural oil production. In large-scale plants a combination of mechanical and chemical extraction (e.g. with hexane as organic solvent) is possible allowing for significantly lower losses in the order of magnitude of roughly 1%. But even then the area specific yield is much lower compared to commonly grown oil crops. Beside this, other non-food oil crops (e.g. camelina) characterised by certain pros and cons are currently under investigation (Neuling and Kaltschmitt, 2014).

Many different projections of how much biomass resources are theoretically available for biofuel provision exist. The only consistency in these studies is that any projection comprises one single element: the consumption of land. Thus in Figure 3 the share of agricultural land in percent of the total land area per region is displayed. For example, related to the year 2011 large variances between the regions become obvious in this graphic. In Oceania, about 21% of the total land is used as agricultural area, whereas in Asia about 53% is utilised as agricultural land (Faostat, 2015).

The fundamental aspects regarding the availability of agricultural land have to be underlined in order to fully understand the land use aspect as a key issue in the production of biofuel. Based on the fact that agricultural land is limited and cannot be extended significantly there is necessarily a competition for agricultural goods between the market for food, the market as a raw material and the energy market (Worldwatch Institute, 2007). The consequence is that the use of land for biomass provision for energy respectively biofuel production
leaves less land available for the growth of food and/or raw material characterised usually by higher market prices. To avoid any problems resulting from this situation e.g. with hunger in certain areas it is essential to ensure sufficient cropland for food production especially taking into account the global increase in population as well as in settlement areas developed on fertile land before enhancing the production of energy crops for e.g. biofuel provision. In many countries worldwide such conflicts are prevented by policies and regulations to avoid the competition between bioenergy producers to seek for high quality land (e.g. high crop yields), and thus, compete directly with food production (Fava Neves et al., 2011). Nevertheless, this issue is still controversially discussed on various scales and no general solution has been developed in recent years.

Land availability, climatic conditions and water restrictions directly correspond to cultivation statistics and projections worldwide. Figure 4 displays exemplarily agricultural areas for selected biomass resources. The total area harvested amounted to 438 million hectares in 1961 and increased up to 614 million hectares in 2013 for the selected agricultural feedstocks.

Figure 5 additionally shows the area specific yields for selected agricultural crops. Thus, between 1961 and 2013 the specific yields of the agricultural feedstocks increased constantly on a global level. For example, the specific yields of sugar cane raised from about 50 to 71 t ha\(^{-1}\) yr\(^{-1}\) and of palm oil fruit from 4 to 15 t ha\(^{-1}\) yr\(^{-1}\). Nevertheless, between neighbouring years there might be significant differences between the specific yields due to flooding or drought, due to insect infestation and other environmental impacts.

Thus, both, the area harvested and the specific yields, increased considerably between 1961 and 2013. The consequence is that the total agricultural crop production also grew dramatically. Figure 6 displays the total production of selected types of biomass between 1961 and 2013.

The recent agricultural outlook gives an impression about the share of biomass (i.e. cereals as the most widely consumed agricultural good including wheat, coarse grains and rice) used as feed, food, for the production of biofuels or other purposes. According to this the amount of cereals produced between 2012 and 2014 sums up to approximately 2400 million tonnes whereof 35% were used as feed, 45.5% as food, 6.25% for biofuel production and 13.25% for other purposes (Organisation for Economic Co-operation and Development, 2015).

### Organic Waste

Biomass referred to as ‘organic waste’ includes a broad variety of very different substances. It covers organic household waste, the biomass-fraction of the municipal solid waste as well as wastes from the food processing industry amongst others. Green waste from public parks or cemeteries as well as garden waste adds up to this. For example, in 2010 a total amount of 108.5 million tonnes of organic waste was produced within the European Union (EU). This includes household yard clippings (19.7 million tonnes), household food waste (4.8 million tonnes) waste form the services industry (12.1 million tonnes) as well as agriculture, forestry and fishing waste (38.8 million tonnes) (Searle and Malins, 2013).

Due to this broad variety and a whole bunch of additional reasons for most types of organic waste the amount which could be utilised in theory for biofuel production is hard to predict. This is related to a whole bunch of different factors. At first the potential is hard to predict since the biomass precipitates decentral and is partly gathered by sanitation departments, private companies or it is simply left on the field. The next problem lies in the provision logistics, which mainly refers to the same points stated before (Valkenburg et al., 2008).

Therefore, to sum up, the organic waste might show a huge potential which is mostly untapped, but which is hard to predict as well as hard to exploit due to numerous restrictions.

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![Figure 3. Agricultural area in % of land area per region (Faostat, 2015).](image-url)
Figure 4. Development of the agricultural area per type of selected biomass resource between 1961 and 2013 (Faostat, 2015).

Figure 5. Specific yield for different agricultural feedstocks (Faostat, 2015).

Figure 6. Total production of selected types of biomass between 1961 and 2013 (Faostat, 2015).
**BIOFUEL PRODUCTION PATHWAYS AND PRODUCTS**

Based on the biomass resources outlined established and emerging processes to produce bio-fuels are described in detail below. Figure 7 gives an overview about these various possibilities currently under development and/or available on the market.

According to these production pathways based on organic material selected secondary energy carriers can be provided. These secondary energy carriers can be biodiesel, hydrocarbons, green-diesel, methanol, ethanol and other alcohols, kerosene/jet fuel, other fuels and fuel additives, bio-methane and synthetic natural gas (SNG) as well as dimethyl ether and hydrogen. The easiest way to use these biofuels is as a drop-in fuel. Hence, they can be used directly in any share together with fossil fuels within the transportation options existing currently within the global mobility sector. But only some of these conversion routes produce fuels which fulfill international fuel standards such as the EN 590 Standard for European diesel fuel (CEN European Committee for Standardisation, 2014b) or the ASTM D7566 Standard for synthetic aviation turbine fuels (American Society for Testing and Materials, 2016). Thus, some of the biofuels enumerated above can undergo a further chemical treatment to ensure that the existing fuel standards are met.

Due to the broad variety of production pathways displayed in Figure 7 merely conversion routes of a selection of pathways is described below. Nevertheless, the selected pathways comprise a broad variety of mechanical, biological, thermo-chemical and chemical process steps and thus, reflect the key development pathways visible on the market as well as in research for the time being.

**VEGETABLE OIL DERIVED FUELS**

Vegetable oils or fats are mainly produced out of oil or fat containing parts of plants, which can be kernels or seeds from rape, sunflower, oil palms, jatropha or camelina as well as fruits or seeds from oil palms or olives (Zimmer, 2010; van der Putten and Jongh, 2010; Shonnard et al., 2010; Carter et al., 2007). This oil or fat production can be done by mechanical solid-liquid separation (i.e. pressing) and/or by extraction (i.e. the extraction of oil/fat out of the cell with an extraction agent, e.g. hexane) (Bockisch, 1998).

The majority of today’s oil production is realised in large-scale oil mills with throughputs up to more than 100 t ha⁻¹. These production plants show more or less the same process sequence. Firstly, the oil is separated from the plant parts and consequently refined and upgraded to the desired degree.
Within such large-scale oil mills the biomass containing oil or fat is cleaned and/or sterilised. Additionally the material is crushed in most cases as well as conditioned (e.g. moisture content, temperature level) to allow for a more easy oil removal. For oilseeds with relatively high oil contents a pressing process is realised removing approximately two-thirds up to three-quarters of the oil contained originally within the biomass. The remaining press cake is then extracted with a solvent recycled internally within the overall extraction process. Two product streams are provided: the extraction oil and the meal (i.e. the remaining basically oil-free biomass). In most cases the oil undergoes a post-treatment directly after pressing and/or extraction to reduce the share of undesired substances, e.g. phosphorous, calcium or magnesium. This includes mainly bleaching and in some cases degumming. Therefore, adsorbent materials and filter aids were mixed into the oil for conditioning of the suspension. Subsequently the additives and the reaction products as well as the solid seed components were separated (Atabani et al., 2013). After this procedure the pre-refined oil can be used for further conversion into a biofuel with clearly defined fuel characteristics based on different conversion routes (Santori et al., 2012).

**FATTY ACID METHYL ESTERS**

Fatty acid methyl ester (FAME) is a mixture of different fatty acid methyl esters. Commonly this mixture is referred to as biodiesel (Hoekman et al., 2012). Compared to pure vegetable oils the chemical structure of biodiesel molecules is closer to those of diesel fuels derived from fossil sources; nevertheless, the diesel fuel standard cannot be met (this is one reason why biodiesel is sold on the market as a mixture with fossil diesel fuel containing usually less than 10% biodiesel) (Refaat, 2009). Thus, FAME is commonly utilised as a partly substitute for fossil diesel fuel (European Biofuels Technology Platform, 2011). Relevant fuel regulations for FAME are: (i) EN 590/AC (CEN European Committee for Standardisation, 2014a), (ii) EN 14 214 (CEN European Committee for Standardisation, 2014b), and (iii) ASTM D 6751 (American Society for Testing and Materials, 2015). The main feedstocks applied for the FAME production process are; (i) pure vegetable oil (e.g. rape, sunflower, soya, palm), (ii) used cooking oil (if available) and (iii) waste animal fat (if available) (European Biofuels Technology Platform, 2011). Vegetable oils mainly consist of triglycerides, *i.e.* molecules with three fatty acid chains attached to the alcohol glycerol. The structure of the fatty acids is always identical; however, depending on the oil crop the hydrocarbon chain length along with location and number of double bonds between carbon atoms within the chain may vary (Patterson, 1983).

Transesterification reduces: (i) the viscosity and (ii) the flash point of (vegetable) oils. This modification of the oil molecule allows for properties close to that of conventional diesel fuel (Demirbas, 2003). Nevertheless, the physical and chemical characteristics of these molecules depend strongly on the type of vegetable oil (Dubois et al., 2007). Figure 8 displays the simplified FAME process. Thus, after a pre-treatment together with a catalyst and methanol the plant oil is converted to biodiesel and glycerol.

The produced biodiesel requires a different set of additives than fossil diesel due to its composition to guarantee accurate low temperature behaviour and to minimise oxidation processes (Ribeiro et al., 2007). Impurities in FAME (*e.g.* metals) should be limited to allow for a long lasting use as a motor fuel without damaging the engine (European Biofuels Technology Platform, 2011).

The use of FAME within existing transportation devices is challenging due to the following aspects: (i) FAME has solvent properties (*i.e.* deposits formed in the fuel-carrying components are dissolved and potentially deposited in the fuel filters), (ii) FAME dissolves plasticiser in plastics, and (iii) FAME is hydrophilic (*i.e.* fuel contamination with water can lead to microbiological contamination, sludge, filter clogging and tank corrosion) (Pearlson, 2011).

The vegetable oil is firstly cleaned from oil-insoluble impurities (*e.g.* seed fragments, meal fines, free water, waxes) via filtration. Afterwards oil-soluble impurities (*e.g.* FFA, phospholipids, other gums) are removed through refining (*i.e.* degumming, primarily to remove phospholipids compounds in the oil) and neutralisation (with

**Figure 8. Fatty acid methyl esters (FAME) process.**

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Vegetable/ plant oil (triglyceride)

Pre-treatment

Mixing → Degumming & neutralisation → Centrifugation

Gums, solid waste

Refined plant oil

Conversion step

Trans-esterification → Ester-washing → Distillation

Biodiesel → Glycerol

Catalyst, methanol → Waste water

NaOH, H₃PO₄, H₂O
alkali solution to react with FFA and form soaps) (Gunstone, 2008).

Then esterification takes place as chemical reaction of two reactants (i.e. typically an acid and an alcohol forming esters as the reaction product). Transesterification implicates shifting one ester into another (Leung and Strezov, 2015). Thus, a glyceride reacts with an alcohol (e.g. methanol) in the presence of a catalyst, forming a mixture of fatty acids esters and an alcohol (e.g. glycerol) (European Biofuels Technology Platform, 2011). Figure 9 shows the transesterification reaction of a triglyceride with methanol in the presence of a catalyst (e.g. sodium hydroxide). The fatty acid chains released from the triglycerides form fatty acid methyl esters in the presence of methanol, whereby glycerol is formed as a co-product (Krahl et al., 2010). To overcome obstacles like slow reaction rates or soap formation during the chemical transesterification, the enzymatic transesterification of vegetable oils gained some attention lately. During this process, the biodiesel is produced through a biological conversion of the vegetable oil by appropriate enzymes, which is seen to show a lower energy consumption and the possibility to utilise low quality feedstocks in comparison to the chemical process. Nevertheless, this process is still under research and in its early phase of realisation (Pourzolfaghar et al., 2016).

A general overview of the process steps is given in Figure 10. Here the fatty acids are separated from glycerol and separately bound to methanol during transesterification. Transesterification is carried out: (i) at temperatures between 50°C to 80°C [i.e. close to the boiling point of methanol (60°C to 70°C)], (ii) at atmospheric or slightly higher pressures and (iii) the process is catalytically driven and controlled (Demirbas, 2003). A strong base or a strong acid can be used as catalyst.

Thus, the production of biodiesel is rather simple from a technical respectively a process engineering point of view. This is the reason why the FAME process allows the construction of small decentralised production units as well as large-scale units. Thus, the transport of raw materials via long distances can be avoided realising the former option and take advantage of economy of scale making use of the latter.

Commercial production of biodiesel via transesterification is state of technology. Most of the globally produced biodiesel is provided based on this technology.

**HYDRO-PROCESSED ESTERS AND FATTY ACIDS**

The hydro-processed esters and fatty acids (HEFA) process converts all kinds of vegetable oil as well as free fatty acids via hydrogenation and isomerisation into long-chain and/or branched hydro-carbons (e.g. diesel, jet fuels) (Pearlson et al., 2013). To some extend wastes like used cooking oil (UCO) and animal waste fats can also be used. The overall process scheme of this process is shown in Figure 11 (Neuling and Kaltschmitt, 2014).

Firstly, the feedstock is cleaned; e.g. caustic soda and phosphoric acid are used for degumming and neutralisation (Nikander, 2008); basically the same pre-treatment processes are implemented as discussed above for FAME. Afterwards the various processing steps are performed; they are displayed in Figure 12 (see also Hilbers et al., 2015).

To convert the triglycerides of the vegetable oil into biofuels under fulfillment of the existing fuel specifications (e.g. ASTM D7566 for jet fuel), esters and double bonds have to be fully saturated with hydrogen (i.e. removal of the double bonds and the oxygen from the plant oil molecule) (Furimsky, 2013). During this esterification process the fatty acids are split up from the glycerol backbone by forming propane (Figure 13). This so called hydrogenation process is supported by catalysts; typically, metal-based catalysts (e.g. NiMo, Al2O3) are used (Kuchling et al., 2013).

Depending on; (i) hydrogen availability, (ii) catalytic materials under operation and (ii) process

![Figure 9. Chemical reaction for the production of methyl esters and glycerol (Leung and Strezov, 2015).](image-url)
conditions, three key reactions can occur to remove the oxygen from the vegetable oil molecule (Tóth et al., 2009) (Figure 13): (i) hydrodeoxygenation (HDO), i.e. oxygen is removed as water depending on the hydrogen availability, (ii) decarbonylation, i.e. carbon monoxide is formed if shortages in hydrogen occur and (iii) decarboxylation, i.e. carbon dioxide is formed when the hydrogen amount is even lower compared to (ii). The latter two reactions should be avoided by supplying always the necessary amount of hydrogen.

Due to the fact that decarbonylation and decarboxylation consume carbon atoms to remove the oxygen (i.e. carbon loss), hydro-deoxygenation is the favourable reaction pathway in this respect. Hydrogenation is an exothermal process taking place at temperatures between 280°C to 340°C and at a pressure of 50 to 100 bar (Myllyoja et al., 2014). Hydrogenation produces both propane as well as linear alkanes in the range of C₈ to C₂₀ depending on the molecular composition of the crude vegetable oil employed. The produced propane is removed from the process and could be sold on the market as ‘green’ propane.

After this hydrogenation step, the fully saturated n-alkanes with a chain length defined by the feedstock properties are isomerised to branched alkanes to lower the freezing point. This will allow fulfilling e.g. the ASTM D7566 specification for synthetic jet fuels (Kasza and Hancsók, 2011). During this isomerisation process a catalyst driven cracking process breaks down long-chain hydrocarbons (n-alkanes) into shorter fragments and in parallel open bounds are saturated with hydrogen and partially recombined fragments to complex branched molecules. The maximum isomerisation yield occurs at temperatures between 280°C and 400°C and a pressure between 30 to 100 bar, depending on the catalyst applied. Zeolite-based catalysts (ZSM) (e.g. Al₂O₃ or Pt) are applicable for cracking and isomerisation (Myllyoja et al., 2014).

The final fuel products can be produced by separation via distillation and rectification (i.e. traditional refinery processes). Thus, a spectrum of various products is provided (e.g. propane, naphtha, diesel, jet fuel).

Under optimal process conditions, e.g. for kerosene production yields of up to 60% correlated
to the overall product spectrum can be achieved. The overall cumulative energy demand e.g. for jet fuel production is stated to be between 1.20 and 1.45 MJ (input)/MJ (output) depending on the type of feedstock and the process design. This directs to an overall kerosene efficiencies of approximately 69% and 83% on an energy basis. The remaining co-products are naphtha, diesel and fuel gas/LPG (Bertelli, 2011).

At present, the plants with the highest installed production capacity (i.e. about 800 000 t yr⁻¹ HEFA products) are located in Singapore and the Rotterdam/Netherlands (Kröger, 2013). Additionally several HEFA-refineries are under construction in West Asia as well as in the US. Since the significance of such hydro-treated vegetable oils especially in terms of the production of green diesel is increasing, recent studies focus on the comparison of such fuels with the well-known ester-type fuels (Glisic et al., 2016).

**CO-REFINING IN CONVENTIONAL CRUDE OIL REFINERIES**

Another possibility to produce fuels from vegetable oil is the co-refining together with fossil crude oil in a ‘classical’ refinery. Although both resources (i.e. vegetable and crude oil) show many similarities concerning the components, they differ in the percentage composition as well as in the molecular structure. As it can be seen from Table 1, the carbon content of vegetable oil is significantly lower than for crude oil, whereas the oxygen content is much higher. The shown bandwidths for crude oil result from the influence of locally varying fractions of light, middle and heavy hydrocarbon contents (i.e. variations between different oil fields). In contrast, the exact composition of vegetable oil depends on the molecule structure of the triglycerides and thereby of the particular plant. In this context, the respective carbon chain length of the bound fatty acids as well as the amount of unsaturated double bonds are decisive (Kaltschmitt et al., 2010).

The major benefit of co-refining of vegetable oil in existing refineries is the availability of existing structures and thereby the possibility to use existing equipment as long as surplus capacities exist and only minor procedural adjustments have to be done. By using the available capacities the feedstock as well as the product spectrum of an existing refinery can be extended. This extension allows a flexible handling of short-term market developments like e.g. the spontaneous increase or drop of vegetable oil prices as well as the possibility to react fast and uncomplicated on a growing demand for biofuels. This increased market flexibility might lead to economic benefits, although high initial investments and generally higher consumption-linked costs due to higher vegetable oil prices have to be taken into...
consideration. In contrast, the operational costs would be more or less the same compared to a simple crude oil refinery.

Besides the economic, procedural challenges such as catalyst deactivation through undesired by-products (e.g. carbon monoxide) or components contained in the vegetable oil (e.g. oxygen) have to be taken into consideration. To guarantee an optimal process management alongside the co-refining, the corresponding problems have been identified now.

Based on this, three different options to utilise vegetable oil as feedstock for a classical refinery can be subdivided. These options are:

- insertion together with crude oil into the atmospheric distillation unit;
- insertion directly to the hydrofiner; and
- insertion directly to the fluid catalytic cracker (FCC) (Mittelmyr and Reichhold, 2009).

All three options show different benefits and drawbacks (Egeberg et al., 2009). So far none of these options has gained market importance because the operator of a refinery acts usually according to the principle: never change a running system. Due to the fact that plant oil contains oxygen responsible for forming water during the hydrogenation process (which is not the case for fossil crude oil) and the possibility that during the hydrogenation carbon monoxide (CO₂) can be formed acting as a catalyst poison, the willingness to co-process crude plant oil and crude fossil oil in one refinery is very limited by the oil industry (e.g. Kaltischmitt et al., 2010).

### ALCOHOL DERIVED FUELS

The alcohol-to-jet process (AtJ) converts alcohols (e.g. ethanol, butanol) derived primarily from sugar and/or starch removed from organic matter into biofuels by modifications of molecules via biological and/or chemical processes. The overall approach is shown in Figure 14. Below firstly the provision of alcohols (i.e. methanol, ethanol, butanol) and based on these alcohols, secondly, the further processing into fuels fulfilling the given fuel standards are discussed in detail.

#### Alcohol Production

Alcohol can be derived from sugar and starch as well as from lignocellulose. Based on these feedstocks methanol, ethanol and butanol can be provided. These alcohols can be used as a biofuel based on different strategies. The easiest way is the use of alcohols (mainly ethanol and butanol) as a fuel (admixture) for ignition engines (Rakopoulos et al., 2010; Wu et al., 2015). In this context, bioethanol is mainly used as blend stock or substitute for gasoline which is then used in spark ignition engines, whereas butanol can be used as blend stock or substitute for diesel in diesel engines. The other possibility is a further processing of the alcohol molecules to produce drop-in fuels which show the same molecular structure and fulfill the same specifications like the equivalent fossil fuels (Weiss, 2011). The later utilisation pathway is described in detail in the following section.

Prior to the conversion to an alcohol a more or less extended pre-treatment step, *i.e.* pressing and extraction and/or milling and grinding takes place (Abubacker et al., 2011; Griffin and Schultz, 2012; Dutta et al., 2011) to unlock the required biomass component. For example, before lignocellulosic biomass can be utilised for an alcoholic fermentation to bioethanol the molecules have to be disaggregated via hydrolysis to receive sugar monomers (Humbird et al., 2011).

![Figure 14. Alcohol-to-jet (AtJ) process.](image-url)
Below the most important pathways to provide alcohol from organic matter are discussed in detail.

**Methanol**

So far methanol is mainly produced via methanol synthesis (Bertau et al., 2014). Feedstock for this synthesis process is synthesis gas containing mainly carbon monoxide (CO) and hydrogen (H₂). This syngas can be produced from biomethane based on a reforming process and/or from solid biofuels via thermo-chemical biomass gasification. Since these two processes utilise very different types of biomass, a broad range of possible conversion routes based on different biomass are available (Hamelink and Faaij, 2002). Alternatively to the heat induced and catalyst driven methanol synthesis syngas can also be converted to methanol based on bio-chemical processes (i.e. syngas fermentation); the latter option is still in an early research status (Griffin and Schultz, 2012). Until today, methanol is mainly produced via a synthesis process based on synthesis gas provided by reforming of natural gas or by gasification of coal (Höhlein et al., 2003). Compared to this the methanol production from biomass isn’t realised in large-scale plants so far. Therefore no reliable efficiency and conversion yield information related to large-scale commercial systems can be given until today.

**Ethanol**

Bioethanol is produced via the ‘classical’ well-known alcoholic fermentation, where sugar molecules are converted into ethanol via microorganisms by splitting off carbon dioxide (CO₂) and releasing thermal energy (Kosaric microorganisms by splitting off carbon dioxide sugar molecules are converted into ethanol via well-known alcoholic fermentation, where commercial systems can be given until today. Conversion yield information related to large-scale plants so far. Therefore no reliable efficiency and production from biomass isn’t realised in large-scale (Höhlein et al., 2003). Compared to this the methanol production from biomass isn’t realised in large-scale plants so far. Therefore no reliable efficiency and conversion yield information related to large-scale commercial systems can be given until today.

**Butanol**

‘Classically’ biobutanol is provided by fermentative pathways like the ABE (acetone, butanol, ethanol) fermentation; the main disadvantages of all these processes and the reason why they are hardly realised for the time being are the poor yields and selectivity to butanol for most of these processes (Tao et al., 2014). Additionally the production of biobutanol uses the same resources as the production of ethanol but the yields are significantly lower and the biocatalysts as well as process technology applied are not fully optimised yet. Therefore yields or conversion efficiencies can hardly be predicted at the time being. Due to the potential advantages of biobutanol related to a further processing to biofuels fulfilling the given fuel standards the butanol-production is subject to many recently on-going research activities (Harvey and Meylemans, 2011).

**FURTHER PROCESSING**

Independently of the alcohol utilised, processes converting alcohols into a drop-in fuel follow in principal mainly follow the same process steps (Atsonios et al., 2015): (i) dehydration, (ii) oligomerisation, (iii) separation and (iv) hydrogenation (Figure 15). The overall goal of these processes is always to remove oxygen from the molecule, combine different alcohol molecules to long-chain hydrocarbons and saturate the most likely existing double bounds with hydrogen. Finally, the provided mixture needs to be separated according to different products to fulfill the given fuel standards.

Within such an overall process, the alcohols are transformed into alkenes in the first place (Takahara et al., 2005; Taylor et al., 2010; Chang and Silvestri, 1977). Then the separation of water via dehydration is performed triggered either by an acid catalytic reaction with sulphuric or phosphoric acid at temperatures around 170°C to 200°C (Wollrab, 2009) or by metal oxide-based catalysts (Breitmaier et al., 2005). Afterwards, the provided short-chain alkenes (i.e. ethene or butene) are merged to longer molecules via catalytic controlled oligomerisation (Froment et al., 1992; Janiak, 2006; Amin and Anggoro, 2002). After a subsequent product separation (i.e. distillation), a final hydrogenation step is realised. Here the unsaturated double bonds are saturated with hydrogen to generate alkanes via a catalytic reaction using Ni, Pt or Pd catalysts at ambient pressure and temperature. An improved performance has been observed by using higher pressure and/or temperature (Breitmaier et al., 2005). The final biofuel yields might consist of 48% kerosene with 35% gasoline and 17% diesel as co-products (Hull, 2012).

This conversion of alcohol based on dehydration, oligomerisation, separation and hydrogenation to long-chain hydrocarbons fulfilling the given fuel standards is until now not commercialised in this process combination. But various pilot and demonstration plants are under operation; e.g. in Stockholm/Sweden a pilot plant is available with a total production capacity of 10 t ha⁻¹ of products
(Hull, 2012) and in Silsbee/USA a demonstration plant is under operation with a total capacity of roughly 290 t ha\(^{-1}\) (Johnston, 2013).

**BIOGAS DERIVED FUELS**

Under anaerobic conditions, organic matter could be transformed within a watery environment by bioconvertants to methane and CO\(_2\) (Wellinger *et al.*, 2013). Beside this, from dry solid biofuels methane production is also possible based on heat induced chemical processes (Basu, 2013). This biogas or bio-SNG can then be purified and used directly within CNG or even LNG vehicles. Additionally, biomethane can be further processed to hydrocarbons liquid under standard conditions. This overall process (in combination with anaerobic digestion) is illustrated in Figure 16 and discussed in detail below.

**BIOMETHANE PRODUCTION**

Biomethane can be produced using two different conversions routes based on very different types of organic feedstock.

**Anaerobic Processes**

In principle, all types of biomass resources can be used for an anaerobic digestion except of wood (*i.e.* lignin is difficult to be converted by the respective bacteria) (Deublein and Steinhauser, 2011). Due to the fact that biological processes need water to operate efficiently typical feedstocks are animal manure, organic waste from the food processing industry, bio-waste from households and sewage sludge. Beside this, energy crops (*e.g.* maize, corn silage) also to be used as a feedstock for biogas plants can be grown on agricultural areas (Am Buswell and Mueller, 1952; Wett and Insam, 2010).

For example, a corn-cob-mix (*i.e.* corn silage) can be cultivated in Germany with an average substrate yield of 45 t ha\(^{-1}\) yr\(^{-1}\) and correspondingly, with a biogas yield of roughly 200 m\(^3\) t\(^{-1}\) sub-strate and a biomethane content of 54% (Fachagentur Nachwachsende Rohstoffe e.V., 2014) a bio-methane yield of 4860 m\(^3\) ha\(^{-1}\) yr\(^{-1}\) can be achieved (Fachagentur Nachwachsende Rohstoffe e.V., 2013). Herbaceous waste from public parks or cemeteries show a substrate availability of 15 t ha\(^{-1}\) yr\(^{-1}\) and a biogas yield of about 98 m\(^3\) t\(^{-1}\) and correspondingly 794 m\(^3\) ha\(^{-1}\) yr\(^{-1}\) biomethane (Fachagentur Nachwachsende Rohstoffe e.V., 2014). Additionally the biogas yield from the different organic waste streams vary significantly depending amongst others on the organic matter content as well as the degradability of the organic material (Li *et al.*, 2013).

The technology for an anaerobic biogas production is commercially available, *i.e.* in Germany more than 9000 biogas plants are currently under operation (European Biogas Association EBA, 2014) based on a huge variety of different feedstocks.

The biogas obtained is water saturated and needs to be cleaned (*i.e.* removal of unwanted impuri-
ties like organic particles and water). Additionally carbon dioxide as well as other unwanted gas components (e.g. H₂S) need to be removed prior to further processing into long-chain hydrocarbons. This can be realised based on adsorption or absorption processes; these upgrading processes are state of technology (Ramaswamy, 2013). The final product is basically pure methane.

**Heat Induced Processes**

Another possibility to produce bio-methane is via biomass gasification and the subsequent methanation of the produced and conditioned synthesis gas (Larson and Katofsky, 1993; Griffin and Schultz, 2012). The thermo-chemical gasification process of solid biofuels into a synthesis gas as well as the subsequent gas cleaning is described in detail in the section fuels derived from lignocelluloses; therefore it is not described in detail here.

The subsequent methanation step for the production of methane from the conditioned synthesis gas is a well-known process developed in the very beginning of the 20th century (Rönsch and Kaltschmitt, 2012). During this catalyst controlled chemical process the CO and the H₂ from the synthesis gas react to methane and water in an exothermic reaction at elevated temperature and pressure (Klasson et al., 1992). After removal of the water the methane is cleaned and can be provided as pure methane. The produced methane is often referred to as synthetic natural gas (SNG) (Kopycsinski et al., 2010). The overall efficiency of such an overall process on an energy basis lies in the range of 60% to 65%.

**PRODUCTION OF LIQUID FUELS**

Similar to natural gas biomethane can be reformed into syngas and then further processed, i.e. syngas is further processed to liquid hydrocarbons via Fischer-Tropsch (FT) synthesis [so called gas-to-liquid (GtL) process] (Dry, 2004). The GtL process was initially developed to utilise natural gas resources (e.g. stranded gas) for the conversion into liquid hydrocarbons (Schulz, 1999). Today, this process is realised within the petroleum industry on a very large-scale.

Firstly, biomethane (CH₄) is converted into a synthesis gas consisting of CO and H₂. Due to the fact that usually pure methane is used the resulting synthesis gas is typically very clean and does not have any unwanted impurities. Possible technical processes for reforming are: (i) steam methane reforming (SMR) with H₂ to CO ratios of 4 to 7, (ii) partial oxidation (POX) with H₂ to CO ratios of 1.6 to 1.9 and (iii) auto-thermal reforming (ATR) with H₂ to CO ratios of 2.2 to 2.3 (de Klerk, 2011) (Figure 17).

Afterwards the synthesis gas is further processed to liquid hydrocarbons via FT synthesis (Steynberg and Dry, 2004; Dry, 2002). The FT synthesis is an exothermal polymerisation process converting H₂ and CO into various types of hydrocarbons and water (Fischer and Tropsch, 1923). During this process the synthesis gas components start ‘growing’ into long-chain hydrocarbons in a catalyst driven chain reaction. The product distribution of this reaction depends on the chain growth probability (i.e. α-value) described by the so called Anderson-Schulz-Flory (ASF) distribution (Flory, 1936; Schulz, 1935). This chain growth probability depends on different process parameters like temperature, pressure and used catalyst material; for small α-values more light products (i.e. short hydrocarbon chains) were produced and for higher α-values the product spectrum shifts to heavier products (i.e. long-chain hydrocarbons) (de Klerk and Furimsky, 2011). In this context low-temperature FT synthesis (LTFT) (Jager and Espinoza, 1995) for the production of heavier products and high-temperature FT...
synthesis (HTFT) for higher yields of lighter hydrocarbons can be differentiated (Maitlis and de Klerk, 2013). To optimise these processes a main research focus lies on the development of new and/or improved catalysts (Davis and Occelli, 2016).

The yield of such a FT synthesis of the provided syngas is a product spectrum consisting of a broad variety of different hydrocarbons (de Deugd et al., 2003). To fulfill the given fuel specification it is necessary to realise a distillation/rectification step to separate the various fuel fractions from each other; this is usually realised with technologies extensively used within existing crude oil refineries. The remaining long-chain components not attributed to the various product streams are usually further processed within a cracking and isomerisation process connected with further hydro-treating (Gambaro et al., 2011). Afterwards the provided products undergo the same treatment as the original liquid products coming from the FT synthesis.

The GtL process is commercially realised in large-scale by various companies (Wood et al., 2012). Thus it can be adapted for biomethane conversion easily. Also the overall process undergoes on-going research to optimise the hole valuechain, a special research interest is seen in the modularisation of FT units and therein the utilisation of micro-reactors (Zhang et al., 2016; Park et al., 2016).

From a systems point of view this pathway could have advantages by utilising biomethane from an anaerobic digestion for the provision of e.g. jet fuel due to the fact that airplanes need liquid fuels and some wet biomass streams (e.g. animal manure, organic household waste) can be treated most easily and efficiently by anaerobic processes. Compared to this the use of biomethane from thermal processes (i.e. SNG) is not that favourable because firstly the solid biomass is converted into a synthesis gas to be further transformed via a FT synthesis to long-chain hydro-carbons (Rytter et al., 2013; Stöcker, 2008; Ail and Dasappa, 2016). The process is divided into the process steps: (i) biomass processing, (ii) gasification, (iii) syngas conditioning, (iv) FT synthesis and (v) product processing (Figure 18).

For the BtL-process basically all different types of solid biomass are applicable; this includes amongst others industrial waste wood and forest residues, wood from SRF and demolition wood (Spath and Dayton, 2003). Additionally other waste streams like municipal solid waste (MSW) can be utilised if the waste contains enough energy (Arena, 2012).

The pre-treatment of the feedstock primarily takes place to ensure that a more or less homogeneous raw material is available for the following process steps (Kumar et al., 2009). This can include mechanical shredding (to obtain a homogeneous grain size) and thermal drying (to increase the calorific value) (Rönsch, 2011). Depending on the gasifier design, the operation behaviour as well as other influencing parameters thermo-chemical pre-treatment processes (e.g. pyrolysis or torrefaction) might be needed (Trippe et al., 2011).

Within the subsequent gasification step the pre-treated solid feedstock is converted into a synthesis gas. Thereby, the macro-molecules contained within the solid biomass are shattered under the influence of heat (temperature range of 800°C to 900°C) and oxygen deficiency. Under these process conditions the main components gained are H₂, H₂O, CO and CO₂. Gasifiers applicable for such a process are: (i) fixed bed, (ii) fluidised bed or (iii) entrained flow gasifiers (Swanson, 2009). A special type, i.e. plasma gasifier, is often used for MSW gasification (Mountouris et al., 2006). The obtained raw synthesis gas has typically a H₂ to CO ratio of e.g. 1.8 depending on feedstock composition and the gasification agent applied (O₂, H₂O). Beside the syngas fraction, long-

**FUELS DERIVED FROM LIGNOCELLULOSES**

**Biomass-to-liquids**

The conversion of solid biomass to liquid fuels is realised within several phases. The solid biomass is converted into a synthesis gas to be further transformed via a FT synthesis to long-chain hydro-carbons (Rytter et al., 2013; Stöcker, 2008; Ail and Dasappa, 2016). The process is divided into the process steps: (i) biomass processing, (ii) gasification, (iii) syngas conditioning, (iv) FT synthesis and (v) product processing (Figure 18).

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![Figure 18. Biomass-to-liquid (BtL) process.](image-url)
chain hydrocarbons (tars) as well as particles and other impurities might occur and can potentially poison the catalysts needed within the subsequent synthesis process steps (Figure 19).

Therefore the synthesis gas leaving the gasifier needs to be cleaned to the ppm or even ppb-range prior to be used within the FT synthesis. Within such a processing step particles (e.g. inorganic mineral materials, ash and unconverted biomass) are removed using electrostatic processes, washing processes with water or special solvents, or separation steps using fabric filters (Stevens, 2001; Hasler and Nussbaumer, 1999; Simell et al., 1996; Cui et al., 2010). The tar fraction can be removed by washing with water or oil solvents and/or by catalytic respectively, thermal processes or a combination of these options. The following processing steps (i.e. FT synthesis) as well as the product separation and upgrading processes are in principle the same as outlined for the bio-GtL process.

The product yields for BtL fuel production corresponding to the syngas obtained are comparable to the GtL process. The FT synthesis as well as the subsequent treatment steps is basically identical for both processes. Nevertheless, the overall efficiency of BtL is lower caused by energy losses during syngas production via gasification [i.e. (i) for syngas cleaning and conditioning solvents for CO₂ separation and desulphurisation need to be provided and (ii) catalysts for the water gas shift reaction to adjust the syngas characteristics to the demands of the FT synthesis are needed] (Hannula and Kurkela, 2013).

The BtL process is certified for commercial use by the ASTM Standard D7566 Annex 1 (i.e. synthetic jet fuel from FTS). Several small laboratory and demonstration plants have been built in the past. Nevertheless, none of them are currently under operation and most of them have been gone bankrupt in recent years. However, some projects for the conversion of MSW are under development (Niziolek et al., 2016), [e.g. a plant in the US with a capacity of 30 000 t ha⁻¹ kerosene or diesel (Fulcrum BioEnergy, 2014)].

**HYDRO-TREATED DEPLOYMERISED CELLULOSIC JET**

The hydro-treated depolymerised cellulosic jet (HDCJ) process converts solid biomass into bio-crude oil via pyrolysis (in the case of HDCJ the pyrolysis is based on known fluid catalytic cracking technology) and upstream processing to liquid fuels (Figure 20) (Hannula and Kurkela, 2013; Jones et al., 2013; Hassan et al., 2016).

Applicable feedstocks are mainly lignocellulosic biomass and thus solid biomass (e.g. forestry and agricultural residues) (Bridgwater, 2012).

Prior to the process the feedstock needs to be pre-treated, i.e. milling and grinding. A drying step might be applied, if necessary. Then the solid biomass is converted into a bio-crude via pyrolysis. This depolymerisation step can be performed for instance via a ‘traditional’ pyrolysis process or via a biomass fluid catalytic cracking (BFCC) process. Typical process conditions are: (i) absence of oxygen, (ii) relatively high temperature and pressure and (iii) the use of catalysts. Subsequent to the pyrolysis step, a separation step occurs to separate reaction water and catalyst material for recycling. The product fractions (i.e. the pyrolysis oil and gas) are separated in the product recovery section, where the oil vapour is condensed and further hydro-processed (Venderbosch et al., 2010; Augustinova et al., 2013). After hydro-treating (i.e. conversion of alkenes to alkanes and desulphurisation reactions)
the products are separated into the preferred product fractions via distillation technologies (Jones et al., 2013).

For the HDCJ process yields of 41% gasoline, 37% diesel and 22% fuel oil are reported (media). Nevertheless, for further processing steps, catalyst material for the fluid catalytic cracking (FCC) as well as hydrogen for fuel hydro-cracking and hydro-treating are required. However, overall efficiencies have not been reported yet. So far no commercial or large-scale industrial plant for HDCJ fuel production is under operation. The only upscaled plant located in Columbus, USA with an annual capacity of 40 000 t yr⁻¹ a has been shut down midst of 2015 due to a bankruptcy case (Biofuels Digest, 2015).

**COMPARISON AND ASSESSMENT**

The production options for biofuels described above are assessed based on the same criteria to allow for a fair comparison. The definition of these assessment criteria take care of the considerable lack of technically detailed and public available data. Thus, only the assessment criteria outlined below are defined and rated with (+) meaning positive, (o) meaning neutral and (-) meaning negative in tendency.

a. Required feedstock. Different conversion processes can be based on different feedstock types. But biomass is not biomass; organic waste for disposal has another ‘value’ compared to biomass containing starch or sugar for the food market. Therefore the assessment criterion is defined as follows:

- organic waste/wood waste/residues are rated with (+) since usually there is no competition with food production and no problems like land use change occur;
- virgin lignocellulosic biomass is rated with (o) because it is widely available and it cannot be used within the food market, but within the market as a raw material for industry like within the pulp and paper industry where an increased energetic use might also cause competition; and
- biomass containing sugar, starch and/or oil is assessed with a (-) because of food competition and possible land use change issues.

b. Process complexity. Usually simple conversion routes with a low complexity are preferred due to technical and economic reasons; thus the more complex a provision chain is the less profitable it is in most cases especially for the production of a commodity. But the process complexity is a relative assessment criterion. Thus, here the FAME process as the most widely used conversion route for biofuel production is used as a kind of reference process. This reference process is rated with a (o) and all

![Figure 20. Hydro-treated depolymerized cellulosic jet (HDCJ) process.](image)

![Figure 21. Process flow sheet of the production of hydro-treated depolymerised cellulosic jet (HDCJ).](image)
other conversion routes will be rated relative to the FAME complexity \(i.e.\) a lower complexity is rated with a (+) and a higher process complexity with a (-).

**c. Market maturity.** This criterion rates the status of technical realisation and market implementation of the production process. If the process is still in the research and development process and far away from large-scale market introduction it is rated with (-). Processes close to market application are rated with (o) and processes already realised in large-scale operations are rated with (+).

**d. Development potential.** The development potential of a conversion pathway allows for statements if the biofuel provision costs can be expected to be reduced in the future. Within this key figure the already available production capacities as well as the status of industrialisation/commercialisation is assessed. Thus, processes available on a large-scale show usually the lowest development potential and thus the lowest reduction potential of the kerosene provision cost. These processes will therefore be rated with (-). Processes characterised by large improvement potentials and thus significant cost reduction potentials are assessed with (+). The remaining conversion options are assessed in between (o).

The comparison of the different provision pathways dominated by differing process technologies made it obvious that the processes show significant differences concerning the actual status of commercialisation. Despite the FAME and HEFA pathway all options need more R&D to allow for a large-scale biofuel production at moderate production costs. The Bio-GtL route as well as the co-refining are a kind of exception; all major parts of this provision chain are available but they have not been demonstrated in a combined use so far. All other processes are not realised in a big-scale industrial application but the technical feasibility has at least been shown in a demonstration plant.

The results of the assessment outlined above can be summarised as follows (comparison is given in Table 2):

- **required feedstock.** In matters of feedstock availability, HDCJ (\(i.e.\) fuels from pyrolysis) and BtL processes are the most promising choices, because all kinds of lignocellulosic biomass can be used (Figure 21). Biomethane production via anaerobic fermentation and further processing to fuels (Bio-GtL) is based on an even broader feedstock variety, including organic waste and other residues characterised by high water content. Thus for these routes no acceptance problems arising from the on-going ‘food versus fuel’ debate are expected. Processes producing fuels from alcohols also have a good feedstock basis since sugar can be produced from starch and sugar containing biomass as well as from lignocellulosic biomass, although this process isn’t realised in large-scale plants today. Since FAME, HEFA and co-refining mostly use vegetable oil, they have the smallest feedstock basis. Aside from fat containing waste and algae discussed as feedstock, vegetable oil still is the mainly used feedstock. Thus these processes lack in using biogenic material which can be used also within the food and fodder market; this might cause controversial discussions within a more and more critical society if such processes are realised on a large-scale.

- **process complexity.** Concerning the process complexity, for the time being mainly the processes based on gasification and pyrolysis are more complex than the FAME route. HEFA and co-refining are only slightly more complex since they are pretty similar to the FAME production. This is due the fact that the FAME, HEFA and co-refining routes use the result of the biosynthesis realised by nature during the plant growth to a maximum extend. All the other processes start usually with the destruction of the organic molecule

<table>
<thead>
<tr>
<th>Required feedstock</th>
<th>Process complexity</th>
<th>Market maturity</th>
<th>Development potential</th>
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<tbody>
<tr>
<td>FAME</td>
<td>-</td>
<td>o</td>
<td>+</td>
</tr>
<tr>
<td>HEFA</td>
<td>-</td>
<td>o</td>
<td>+</td>
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<tr>
<td>Co-refining</td>
<td>-</td>
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<td>Alcohol derived fuels</td>
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<td>o</td>
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<tr>
<td>Bio-GtL</td>
<td>+ to o</td>
<td>-</td>
<td>o</td>
</tr>
<tr>
<td>BtL</td>
<td>+ to o</td>
<td>-</td>
<td>-</td>
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<tr>
<td>HDCJ</td>
<td>+ to o</td>
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Note: FAME - fatty acid methyl ester.
HEFA - hydro-processed esters and fatty acids.
Bio-GtL - biogas-to-liquid. HDCJ - hydro-treated depolymerised cellulosic jet.
BtL - biomass-to-liquid.
(+)=positive, (o)=neutral, (-)=negative, (x)=no data available.
and then re-synthesise them to fulfill the given fuel standards. This is why the Bio-GtL process and the production of fuels from alcohols are more complex than the FAME process, but not as complex as BtL or HDCJ.

- market maturity. The FAME process is the most market mature of all discussed processes, since it is used for the production of biodiesel for years. The only other up-scaled process is the HEFA process which is realised in different industrial scale plants to produce different types of liquid biofuels. The Bio-GtL process is seen to be the next process ready for market introduction, also different constraints have to be overcome. This is also true for the co-refining, which has some drawbacks in terms of catalyst deactivation and feedstock price. The other three processes (i.e. alcohol derived fuels, BtL, HDCJ) need even more time and research activity to realise an up-scaled market introduction.

- development potential. From a technical point of view, only FAME, HEFA and the GtL process based on natural gas are already available on a commercial basis on the large-scale; all other technologies still have to realise more or less research, development and demonstration efforts. Of all discussed processes the FAME route is surely the most commercially implemented conversion pathway for the time being, directly followed by the HEFA route. Even though fuels based on the FT synthesis are able to produce biofuels fulfilling the given standards, Bio-GtL and BtL plants are not available in industrial scales today. Since the biomass gasification still has some challenges to overcome, it is seen to have a high development potential. This is also true for fuels derived from alcohols or pyrolysis intermediates.

This investigation shows that a lot of activities are on-going to pave the road for efficiently providing biofuels, especially those types of biofuels fulfilling the given standards. Nevertheless, so far no pathway without considerable reservations except from the FAME process can be observed. All other options under discussion show more or less huge advantages as well as significant drawbacks. This is true for the feedstock basis, the process engineering as well as the economic and probably also the environmental performance (not discussed in this article). Thus, the development during the years to come will show which pathway can exploit the still given development potential to overcome these challenges and to contribute significantly to a more environmentally sound biofuel provision. To support and accelerate this development process more R&D activities are needed to perform a big step towards ‘green’ mobility.

FUEL MARKETS

Obviously, the biofuel market is part of the overall market for energy as well as the global market for food and fodder. Thus, the biofuel market is influenced by a broad variety of parameters including the following aspects (BP, 2015b; ExxonMobil, 2016):

- population growth up to 8.7 billion in 2035 and thus, growing demand for food;
- increase in income per person as well as gross domestic products (GDP) due to a strong raise in productivity (e.g. the average level of productivity is expected to decrease in China from 7% p.a. to 4% p.a. and in India from 6% p.a. to 5% p.a. until 2035);
- tendency to a higher share of green chemistry and thus an increased need for organic material to provide, e.g. bulk chemicals; and
- standards of living increase in average within the non-OECD countries.

Most likely these developments will have rising biomass and thus biofuel prices as a consequence. Thus, for the biomass and biofuel price rising price fluctuations can be expected on the medium to long-term. But there are multiple key sources of uncertainty in global production predictions for biofuels and thus also the necessary amount of biomass, including: (i) limited project development capacity, (ii) infrastructure constraints (e.g. developing export pipelines, terminals and water injection infrastructure) as well as (iii) security challenges and political constraints (Finley, 2012).

Also the overall consumption of liquid (and gaseous) energy carriers for transportation purpose will be restrained/effect by a broad variety of aspects including (Finley, 2012):

- surging or falling crude oil and/or natural gas prices;
- new policies and political strategies seeking to improve the efficiency of consumption (e.g. revenue requirements, energy security concerns and sustainable development);
- the further role of electric driven vehicles within the global transportation system;
- the contribution of transportation options operated by hydrogen; and
- shifts of oil to gas within the transport sector, in power generation, industrial applications, as well as in commercial use.

Globally, total oil and biofuel production is expected to increase to meet the future growth in fuel consumption. According to Figure 22, the total oil production in ‘West Asia’ (i.e. up to 1566 million tonnes oil equivalents in 2035) and ‘North America’ (i.e. up to 1203 million tonnes oil equivalents in 2035) will rise significantly compared to ‘S & C
America’ (i.e. 607 million tonnes oil equivalents in 2035), ‘Africa’ (i.e. 440 million tonnes oil equivalents in 2035), ‘Asia & Pacific’ (i.e. 379 million tonnes oil equivalents in 2035) and ‘Europe & Eurasia’ (i.e. 818 million tonnes oil equivalents in 2035).

The annual growth rate is expected to decrease for ethane/LPG, gasoline, jet/kerosene and diesel between 2020 to 2040 compared to the time span between 2013 and 2020. Contrarily, the growth rate of naphtha is estimated to increase. In summary, the transportation fuel demand is predicted to decrease globally within the years to come.

A review and outlook until 2035 of the total liquid energy carrier consumption worldwide per region is given in Figure 23.

The total liquid consumption is projected to increase more rapidly in ‘Asia Pacific’ (i.e. 2013 million tonnes oil equivalents in 2035) compared to ‘West Asia’ (i.e. 576 million tonnes oil equivalents in 2035), ‘S & C America’ (i.e. 440 million tonnes oil equivalents in 2035) and ‘Africa’ (i.e. 288 million tonnes oil equivalents in 2035). The total liquid consumption has already peaked in ‘Europe & Eurasia’ (i.e. 1128 million tonnes oil equivalents in 1990) and ‘North America’ (i.e. 1130 million tonnes oil equivalents in 2005) and it is likely that it will not again reach the level seen in 1990 and 2005.

Figure 24 shows the recent development of the global biofuel production in million tonnes oil equivalents. The largest amount of biofuels until today is produced in ‘North America’ with up to 31 million tonnes oil equivalents followed by ‘S & C America’, ‘Europe’ and ‘Asia Pacific’ with 20, 12 and nearly 8 million tonnes oil equivalents, respectively. ‘Africa’ and the ‘West Asia’ only show marginal amounts of biofuel produced in the last decade.

The global biofuel production is expected to exceed 132 million tonnes oil equivalents in 2035 (BP, 2015b). Figure 25 shows predictions for 2035 for ‘West Asia’ of only marginal biofuel production whereas for ‘North America’ it is assumed to increase up to 49 million tonnes oil equivalents, in ‘S & C America’ about 41 million tonnes oil equivalents, in ‘Asia & Pacific’ about 23 million tonnes oil equivalents, in ‘Europe & Eurasia’ about 15 million tonnes oil equivalents and in ‘Africa’ about 5 million tonnes oil equivalents. Thus, an increase of more than 100% can be expected within the two decades to come according to these assumptions.

Summarised, the (bio-)fuel market shows the following trends; (i) regional energy imbalances will increase until 2035 with significant influence in energy trade, (ii) ‘Asia and Pacific’ will continue to expand their energy imports, (iii) in 2035 ‘West Asia’ will still be the biggest exporter of fossil fuels (BP, 2015b), (iv) biofuels will still only play a neglectable role within the global transportation sector in 2035; this might not be true on a local/regional level (e.g. due to the local frame conditions like for example in Brazil) and (v) the role of biofuels will still be mainly defined by political / administrative measures.

**FINAL CONSIDERATION**

Biofuels are an important and widely discussed option to contribute to a more sustainable transportation sector. Manifold expectations are linked to these options covering technical, economic, environmental as well as social aspects. In contrast to that, within parts of our global society the production and use of biofuels is very much questioned due to potential land use change effects, increasing food and fodder prices, loss of biodiversity and other environmental and societal constraints. Thus, there is no black and
Figure 23. Review and outlook of the total liquid energy carrier consumption worldwide per region (oil, biofuels, gas-to-liquids and coal-to-liquids are included (BP, 2015b).

Figure 24. Total biofuel production between 2004 and 2014 (BP, 2015a).

Figure 25. Expected total biofuel production up to 2035 (BP, 2015b).
white answer about the chances and limitations of biofuels on a global scale. Relevant factors and aspects related to this discussion are listed below.

(i) Global fuel consumption within the transportation sector is projected to continuously increase, driven by rapidly growing economies such as China and India with even disproportionately expanding wealthy middle class. If due to policy measures the relative share of biofuels within the global transportation sector remains constant in the years to come a significant increase would result in absolute terms. Thus, it is likely that the amount of biofuels will increase in the years to come on a global scale.

(ii) Globally there is a trend towards more environmentally sound transportation systems especially on the background of the bad air quality in most of the megacities of the emerging countries. Thus, the reduction of particulate matter emissions within the very dense populated megacities is a strong driver pushing towards a higher degree of sustainability in this area and thus for an increased use of biofuels. It remains to be seen if this development will be overrun by the implementation of electric driven cars and/or the implementation of CNG/LNG within the transport sector.

(iii) After the compromise in Paris/France by the end of 2015, the global warming issue has again moved upwards on the political agenda on a global scale. If the agreement signed in Paris will be ratified by most nations globally and actions will follow it is most likely that biofuels will gain more importance within the transportation sector. This is due the fact that a reduction of GHG emissions with biofuels is easily possible based on existing technology on the production side as well as the end use side under using additional most welcome side effects (e.g. generation on labour, generation of income in rural areas).

(iv) In many developing countries limitations in infrastructure, well-trained labour and limited financial capabilities need to be overcome to support the distribution of biofuel production. Nevertheless, due to a growing world population and thus a strong increasing food demand these challenges have to be overcome anyway. And a growing biofuel market could help to generate income to contribute to an increased development especially in rural areas.

(v) The social acceptance of biofuels especially in industrialised countries with very active NGO’s strongly influencing the public opinion is limited. Thus, political measures supporting biofuels should always integrate a land use and a rural development strategy dedicated towards a more sustainable development. Such a strategy could be successful. Today biomass dedicated to be used for biofuel production already has to fulfill demanding sustainability criteria so that the product can be accepted as a biofuel according to law within the European Union. This has helped to create acceptance.

(vi) The globally available biomass resources provide a considerable potential for biofuel production. The primarily feedstock of choice should be agricultural and forestry residues, because this organic matter is immediately available and does not require additional land cultivation and does not cause direct or indirect land use change. The consequence would be to develop efficient biofuel provision chains able to use such residues with high priority. Thus, a boosted technology development should be realised targeted especially towards such organic material.

(vii) Lots of different technologies are available or under development to provide biofuels based on very different types of organic matter. All of these processes show partly considerable losses. Thus, the overarching development goal of the years to come is to reduce these losses based on improved process technology as well to new and more efficient processes. This would also help to increase the public acceptance of biofuels within a more and more technology critical society at least within the highly industrialised countries.

(viii) The available conversion pathways are at very different stages of commercial development. These differences can be expressed by the so called Technology Readiness Levels (TRL) representing a type of measurement system employed to evaluate the maturity level of a technology. Each technology is evaluated against the parameters for each technology level and is subsequently assigned a TRL rating based on the projects progress (NASA, 2015). The distribution of TRL values achieved for each conversion pathway is shown in Figure 26. Based on this most of the conversion routes outlined above are still on a very low TRL. If biofuels should contribute with higher shares within a globally strongly growing mobility sector they have to move fast towards higher TRL. Thus, it is the task of various governments to define the political guardrails to make this happen. Additionally this technology development should be safeguarded by public R&D funds to reduce the costs (and resource demand) of the various conversion technologies.
(ix) So far biofuels can compete on the energy markets on the background of cheap fossil fuels (ca. 30 USD per barrel, February 2016) only under very promising frame conditions and/or based on political measures. To improve this situation it is essential that the biofuel provision costs are further reduced. The main option is to develop processes for biofuel provision towards biorefinery processes characterised by the avoidance of waste products as well as the provision of a manifold of other high value products to be sold as a raw material (e.g. bulk chemicals, pharmaceutics, cosmetic products).

(x) Prices on the international stock exchange for agricultural commodities vary significantly. Here the biofuel market could act as a kind of buffer because biofuels and fossil fuels are easily exchangeable depending on the actual market situation. If the prices for agricultural products are low parts of the surplus production could go into the fuel market. If the situation is the other way round biofuels could be substituted by fossil fuel. If the globally valid and accepted frame conditions support such a scheme biofuels could even contribute to global food security due to more predictable prices. Thus, on a global level the frame conditions should be adjusted so that the use of biofuels contributes to food security and not the other way round.

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