



Biofuels: Types and Process Overview

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Abstract

The term biofuels refer mainly to fuels derived from biomass, which can be considered as plants and organic residues. In this chapter attention will be focused on liquid biofuels that can be used mainly for transportation. As reported in the IEA Technology Road Map for biofuels, presented in 2011, they can be divided in two main categories, based on the type of technologies used: conventional biofuels (sugar- and starch-based ethanol, conventional biodiesel, biogas) and advanced biofuels (cellulosic ethanol, hydrotreated vegetable oil, biomass-to-liquids, biosynthetic syngas, etc.). The production of these biofuels is object of big research efforts directed through process intensification and increase of the efficiency of biomass conversion into an energy vector. For this reason this chapter takes into account the production of first-generation biodiesel, first-generation bioethanol, second-generation biodiesel, second-generation bioethanol, and hydrotreated vegetable oils focusing on their market and the most importantly production techniques.

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Keywords

Biofuels · Biodiesel · Bioethanol · Vegetable oils · BTL · Fischer-Tropsch

1.1 Introduction to Biofuels

Compared to gasoline, diesel, and natural gas, alternative liquid biofuels derived from biomasses have one main selling point: they are renewable. While there are significant differences among liquid biofuels with regard to production, all are argued to have a lower environmental impact at both the extraction and consumption stages (Renewable Fuels Association 2015; Skutsch et al. 2011; Slade and Bauen 2013). Thus, while biofuels are economically marginal in the marketplace, they are socially and politically useful (Solomon et al. 2007).

The major benefits of biofuels by an economic, environmental, and energetic point of view are shown in Table 1.1.

Biomasses, based on their composition, can be divided into three main categories: sugar/starch crops, lignocellulosic biomass, and oil plants. The composition and main characteristics of these feedstocks will be better explained in the next paragraph. Figure 1.1 shows the most important conversion processes to produce biofuels from biomass. From sugar/starch crops, bioethanol can be produced through milling, hydrolysis, fermentation, and refining. Bioethanol can be also produced with similar processes from lignocellulosic materials. Lignocellulosic biomass can

Table 1.1 Benefits linked with the use of biofuels (Demirbas 2009a)

Economic impacts	Sustainability
	Fuel diversity
	Increased number of rural manufacturing jobs
	Increased income taxes
	Increased investments in plant and equipment
	Agricultural development
	International competitiveness
	Reducing the dependency on imported petroleum
Environmental impacts	Greenhouse gas reductions
	Reducing of air pollution
	Biodegradability
	Higher combustion efficiency
	Improved land and water use
	Carbon sequestration
Energy security	Domestic targets
	Supply reliability
	Reducing use of fossil fuels
	Ready availability
	Domestic distribution
	Renewability

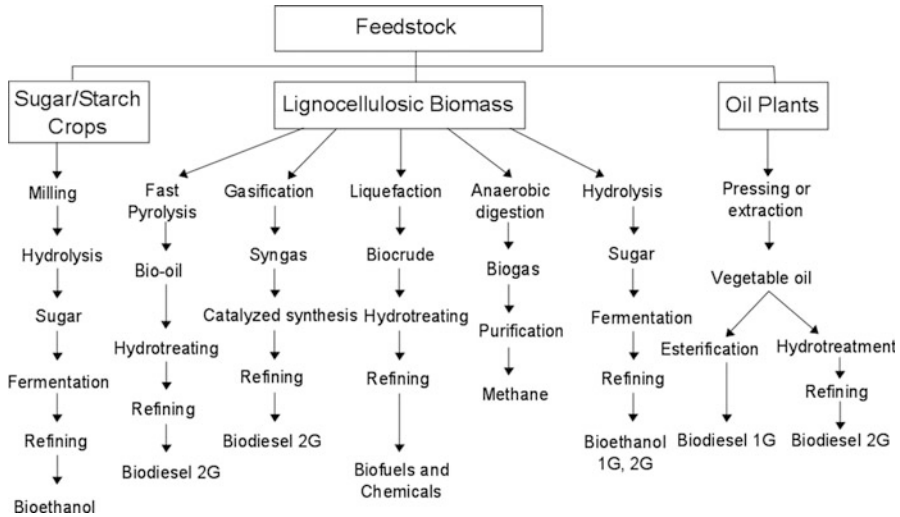


Fig. 1.1 Most important conversion processes to produce biofuels from biomass (Demirbas 2009b)

be converted also through pyrolysis, gasification, hydrothermal liquefaction, and anaerobic digestion. Vegetable oils can be converted through transesterification but also through hydrotreating, producing hydrotreated vegetable oils. This chapter will take into consideration the following biofuels:

- Biodiesel
- Bioethanol
- BTL (Biomass to Liquids)
- HVO (Hydrotreated Vegetable Oils)

These have been selected among the existing ones because they are believed to have higher market potential.

As it is reported in the World Energy Outlook 2018 of the International Energy Agency (IEA), transport accounts for a fifth of global energy demand and is responsible for a quarter of energy-related CO₂ emissions. More than 95% of today's transport sector emissions are from oil (IEA 2018) and the demand for the transport of people and of goods is projected to increase significantly through to 2040.

Global transport biofuel consumption has increased by more than 5% in 2017 and has reached 150 billion liters, of which three-quarters is ethanol. In energy terms, biofuel consumption is about 86 Mtoe, of which two-thirds is ethanol. Biofuel promotion policies are now in place in 68 countries. While large volumes of advanced biofuels could be produced sustainably, their development has been slowed by their costs. In fact, producing a barrel of second-generation biodiesel can cost around \$140/barrel today (IEA 2018). Assuming that advanced biofuels are not responsible of net CO₂ emissions, a carbon tax above \$150 per ton of CO₂ would

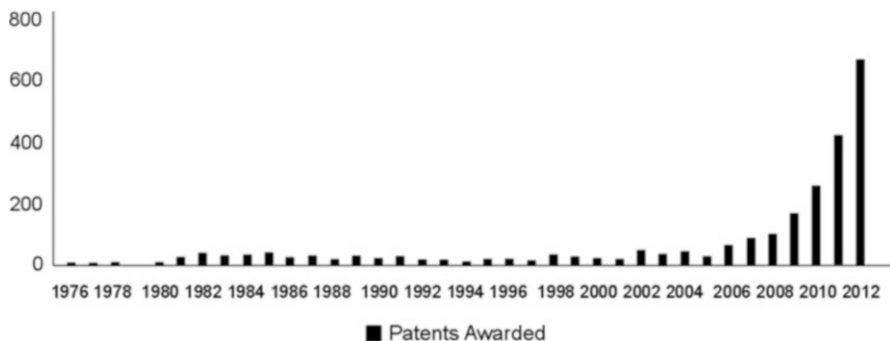


Fig. 1.2 Patents awarded for all biofuels technologies, $N = 2587$ (Arnold et al. 2019)

be required for them, to be cost-competitive with fossil ones (IEA 2018). Production costs have to be reduced through technological innovation. Continuous innovation must provide constant or increasing returns to innovative efforts, but complexity can increase the costs of those efforts (Costantini et al. 2013, 2015a). In the analysis of (Arnold et al. 2019), an innovation is considered to be a technical novelty that earns a patent. Using the data provided by the United States Patent and Trademark Office (USPTO), a database of liquid biofuel technologies patented since 1976 has been constructed (Arnold et al. 2019).

Figure 1.2 shows that biofuel technologies of all generations show a low level of innovation from the start of the data series through 2005, while from 2006 the level of innovation has risen and continues to rise consistently. This rise in patenting parallels the results seen in other international studies. In fact, biofuel patents rose first in Japan, in the period 1994–2002, and then increased in Europe in 2004 and in the United States in 2005 (Albers et al. 2016). The reasons for this increase can be found in market forces, concerns over supply, price, and air quality.

From 1976 through 2012, the number of patents per author has declined from 0.64 patents per author in 1976 to 0.33 patents per author in 2012. Thus it can be concluded that the productivity of innovation in biofuels has also declined. Besides, the increase in patenting from 2006 on did not affect the trends in patents productivity. The decline of productivity of innovation is evident in both newer technological areas (such as information technology, biotechnology, and nanotechnology) and in older sectors (Strumsky et al. 2010; Tainter et al. 2018). This appears to be the result of increasing complexity in the research process (Strumsky et al. 2010; Tainter et al. 2018). As Kessler and Sperling (Kessler and Sperling 2016) noted, second-generation biofuel technologies are surely more complex than those first-generation ones (Himmel et al. 2007). This implies that nowadays biofuel innovation requires increasing diversity of technical knowledge and a multidisciplinary approach. It is now difficult for a single researcher to master all of the technologies that make up a biofuel patent (Costantini et al. 2015b). As a result, it requires the collaboration of increasing numbers of researchers to develop a patent, who work in interdisciplinary teams (Albers et al. 2016).

1.2 Feedstock

1.2.1 Vegetable Oils

The main feedstock for first-generation biodiesel production worldwide includes oils from energy crops (such as soybean, rapeseed, canola, sunflower, corn, palm kernels, animal fats) and recycled oil. *Jatropha curcas L.* oil has also been used for biodiesel production in tropical areas such as India and Africa.

Vegetable oils from energy crops (which are also often commercialized in the food sector) are considered high-quality materials for biodiesel production because they have a high triglyceride content (92–99%) and low FFA content (<2%). Vegetable oils produced from soybean and rapeseed are the most commonly used feedstock for biodiesel production in the United States and Europe, respectively.

Waste oil is recycled cooking oil used in restaurants, food industry, and households. It contains usually more free fatty acids and water and less triglycerides than fresh vegetable oils. The typical composition of waste oil includes linoleic acid (53%), oleic acid (28%), and palmitic acid (11.73%) (Shah et al. 2007). Because of its high FFA concentration and water content, waste oil usually needs a pretreatment to remove water and transform FFAs to esters. The production of waste oils worldwide is significant; in 2007, in fact more than 15 million tons have been generated in the world (Gui et al. 2008). Vegetable oils composition and main characteristics are proposed in Table 1.2 (Leung et al. 2010).

1.2.2 Starch and Sugars

Ethanol derived from biomass has the potential to be a sustainable transportation fuel that can replace gasoline (Wang 2000; Kim and Dale 2004). Ethanol can be produced from sugar- or starch-containing crops (see Table 1.3) and lignocellulosic biomass (such as agricultural residues, herbaceous crops, forestry wastes, wastepaper, and other wastes) (Wyman 1996). The production of bioethanol from lignocellulosic biomasses is still under development. The composition of lignocellulosic biomasses is presented in the next paragraph.

1.2.3 Lignocellulosic Biomass

Lignocellulosic biomass composition derives directly from the composition of the plant cell wall (Caffall and Mohnen 2009). The lignocellulosic feedstock is represented by the agricultural and forest residuals, which are mainly composed by the cell wall tissue, which remains after the plants have died. Plant cell wall biomass contains mainly cellulose, hemicellulose, and lignin. Different species of plants have significant differences in the proportions of the main components and important differences in the types of hemicellulose which are contained and the ratios of

Table 1.2 Feedstock for biodiesel production (Leung et al. 2010)

Type of oil	Species	Fatty acids composition (wt. %)	Kinematic viscosity (cst. at 40 °C)	Acid value (mg KOH/g)
Edible oil	Soybean	C16:0, C18:1, C18:2	32.9	0.2
	Rapeseed	C16:0, C18:0, C18:1, C18:2	35.1	2.92
	Sunflower	C16:0, C18:0, C18:1, C18:2	32.6	–
	Palm	C16:0, C18:0, C18:1, C18:2	39.6 ^a	0.1
	Corn	C16:0, C18:0, C18:1, C18:2, C18:3	34.9 ^a	–
	Canola	C16:0, C18:0, C18:1, C18:2, C18:3	38.2	0.4
Nonedible oil	Jatropha curcas	C16:0, C16:1, C18:0, C18:1, C18:2	29.4	28
Other	Used cooking oil	Depends on fresh cooking oil	44.7	2.5

^aKinematic viscosity at 38 °C, mm²/s

Table 1.3 Starch content in energy crops used for 1st generation bioethanol (Zabed et al. 2017)

Crop	Scientific name	Starch content (%) ^a
Corn	<i>Zea mays</i>	70–72
Sorghum	<i>Sorghum bicolor</i>	68–70.7
Wheat	<i>Triticum aestivum</i>	65.3–76
Rice	<i>Oryza sativa</i>	87.5
Oat	<i>Avena sativa</i>	65.6
Potato	<i>Solanum tuberosum</i>	73

^aDry weight

monomers in lignin (Pauly and Keegstra 2010). The composition in terms of main components of the most important lignocellulosic feedstocks is shown in Table 1.4.

Woody biomass contains more cellulose and lignin, whereas grass biomass has higher content of hemicellulose (mainly xylan), extractives, and ashes.

Cellulose is a polysaccharide consisting of a linear chain of D-glucose units.

Hemicellulose has a backbone composed of 1, 4-linked β -D-hexosyl residues and may contain pentoses, hexoses, and/or uronic acids. Other sugars, such as rhamnose and fucose, may also be present, and the hydroxyl groups of sugars can be partially substituted with acetyl groups (Gírio et al. 2010). Unlike cellulose, hemicellulose composition varies depending on cell tissue and plant species (Chundawat et al. 2011). In fact it can be noted that:

- The principal hemicellulose of hardwoods is an O-acetyl-4-O-methylglucuronoxylans.
- The main hemicellulose of soft woods is an O-acetylgalactoglucomannan.

Table 1.4 Main chemical composition of some lignocellulosic feedstocks (Zhao et al. 2012)

Feedstock	Cellulose (%)	Xylan (%)	Galactan (%)	Araban (%)	Lignin (%)	Mannan (%)	Extractives (%)	Ash (%)
Hybrid poplar	48.6	14.6	0.3	0.3	21.8	0.5	NA*	0.7
White oak	43.6	18.0	0.4	2.4	23.2	2.9	NA	0.6
Red oak	43.4	18.9	NA*	1.9	25.8	2.7	NA	NA
Walnut	46.2	16.5	NA	1.8	21.9	2.6	NA	NA
Maple	44.9	17.3	NA	2.8	20.7	2.9	NA	0.4
Corn stover	40.9	18.0	1.0	3.0	16.6	0.6	7.3	9.7
Wheat straw	38.2	21.2	0.7	2.5	23.4	0.3	13.0	10.3
Rice straw	34.2	24.5	NA	NA	11.9	NA	17.9	16.1
Switchgrass	31.0	20.4	0.9	2.8	17.6	0.3	17.0	5.8

*NA: data not available

- The main hemicellulose in Gramineae (such as cereal straws) is arabinoxylans, which are similar to hardwoods xylan, but the amount of L-arabinose is higher (Peng et al. 2011).
- Lignin is the organic substance which is responsible of binding the cells (Sticklen 2008). The three basic monomeric units constitute lignin: p-Hydroxyphenyls (H); Guaiacyls (G); Syringyls (S).

Hardwood lignins are predominantly G and S monolignols with trace amounts of H units. Soft wood lignins are composed of mostly G units. Herbaceous plants contain all three units in significant amounts (Chundawat et al. 2011; Buranov and Mazza 2008).

1.3 First-Generation Biodiesel

1.3.1 Transesterification Reaction

The transesterification reaction with alcohol is represented by the general equation shown in Fig. 1.3a which consists of a number of consecutive, reversible reactions. These are shown in Fig. 1.3b. The first step is the conversion of triglycerides into diglycerides, and then diglycerides are converted into monoglycerides and monoglycerides into FFAs and glycerol. Each step yields one methyl ester molecule (Freedman et al. 1986; Nouredini and Zhu 1997). The transesterification can be both catalyzed by acid and alkali.

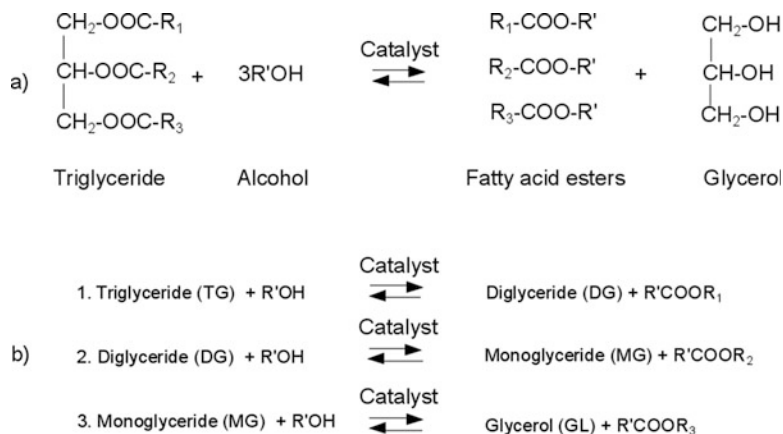


Fig. 1.3 Transesterification reaction (Eckey 1956)

Different types of catalyzed transesterification can be adopted (Lam et al. 2010):

1. Homogeneous base catalyst
2. Heterogeneous base catalyst
3. Homogeneous acid catalyst
4. Heterogeneous acid catalyst
5. Enzymes

State-of-the-art biodiesel production usually is done using base catalyst (e.g., KOH or NaOH). In that case reaction time can vary between 0.33 and 2 hours and yields are between 88% and 98% (Lam et al. 2010; Liu et al. 2010). Catalyst loading is between 1 and 6%wt, while methanol excess is between 7:1 and 9:1, expressed in molar ratio. Temperature can range between 60 and 87 °C (Lam et al. 2010). Also two-step catalysis can be a solution: first acid catalyst, then followed by basic catalysis.

Homogeneous acid catalyst usually can use H₂SO₄ or HCl. Heterogeneous basic catalysis can be performed using basic zeolites, alkaline earth metal oxides (e.g., CaO), and hydrotalcites. Heterogeneous acid catalyst can be zirconium oxide (ZrO₂), titanium oxide (TiO₂), tin oxide (SnO₂), zeolites, sulfonic ion-exchange resin, sulfonated carbon-based catalyst, and heteropoly acids (HPAs) (Lam et al. 2010).

Enzyme catalysts lipases can be produced from several microorganisms, such as *Mucor miehei* (Lipozyme IM 60), *Pseudomonas cepacia* (PS 30), *C. antarctica* (Novozyme 435), *Bacillus subtilis*, *Rhizopus oryzae*, and *Penicillium expansum* (Lam et al. 2010; Liu et al. 2010, 2011a, b; Yan et al. 2014; Fan et al. 2016, 2017; Su et al. 2016; Li et al. 2017).

1.3.2 Biodiesel Production Process Diagram

Figure 1.4 shows the flow sheet of the production processes used for biodiesel.

Based on Fig. 1.4 scheme, it is assumed that alcohol, catalyst, and oil are inserted in the reactor and agitated for approximately 1 h at 60°C. Small plants often use batch reactors (Stidham et al. 2000), while larger plants (higher than 4 million liters/year) use continuous stirred-tank reactors (CSTR) or plug flow reactors operated in continuous mode (Assman et al. 1996).

Once methyl ester has been produced, it must be separated from the glycerol (through phase separation because glycerol is much heavier). Methyl esters undergo a neutralization step and then pass through a methanol stripper. A vacuum flash process or a falling film evaporator can be used for this purpose. Before washing with water, acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps react with the acid to form water-soluble salts and FFAs. The salts are removed during the water washing step. The water washing step removes traces of catalyst, soap, salts, methanol, or free glycerol remained in the biodiesel. After the wash process, remaining water is removed from the biodiesel by flash-vacuum distillation.

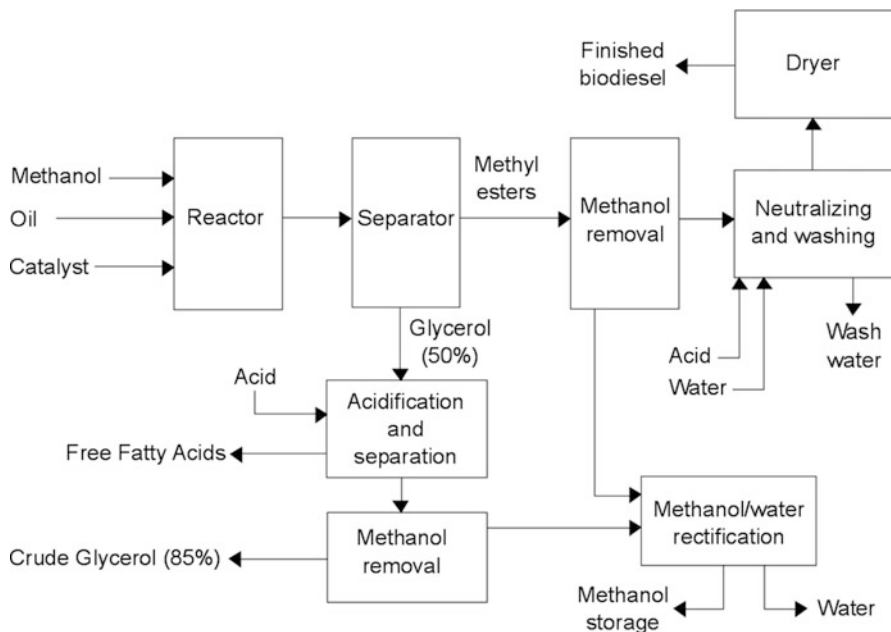


Fig. 1.4 First-generation biodiesel production flow sheet (Van Gerpen 2005)

The glycerol stream leaving the separator is composed only by about 50%wt glycerol. It contains also methanol, catalyst, and soap. The first step in glycerol refining is to add acid to split the soaps into FFAs and salts. The free fatty acids are not soluble in the glycerol and will rise to the top, so that they can be removed and recycled. The salts generally remain with the glycerol. The methanol mixed with the glycerol is removed by flash-vacuum distillation or conventional distillation. A purity of approximately 85% is reached; this allows to sell the glycerol to a refiner. Glycerol refining can be performed using vacuum distillation or ion exchange processes. A purity comprised between 99.5%wt and 99.7%wt is achieved.

The methanol that is removed from the methyl ester and from glycerol is mixed with water after separation has been performed. This water should be removed in a distillation column before the methanol is recycled into the process.

1.4 Bioethanol

1.4.1 Production of Ethanol from Sucrose

Sugar cane, sugar beet, and sweet sorghum are crops which contain sugars, which can be used as feedstock for ethanol production. Their main advantages are high yield of sugar per hectare and low conversion costs.

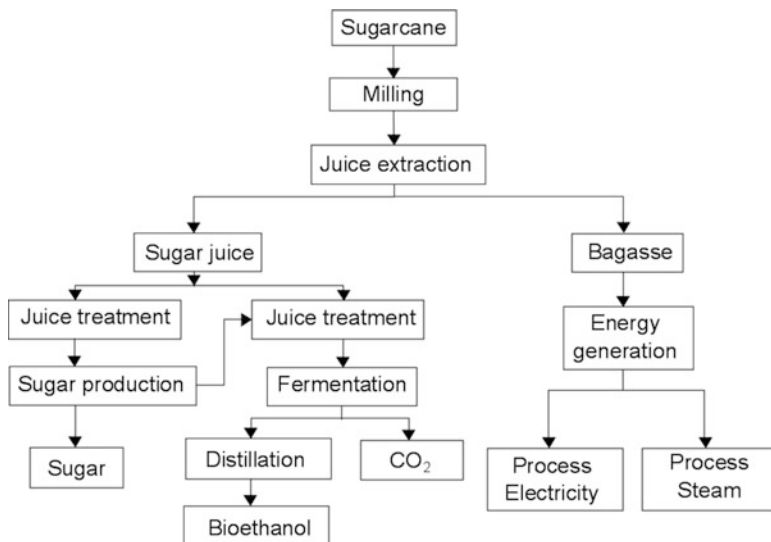


Fig. 1.5 Bioethanol production from sugar juice (Vohra et al. 2014)

Sugarcane has become a very effective source of biofuel, given that:

1. Bagasse can be used to generate process steam and electricity.
2. Vinasse (the liquid effluent) can be used as a fertilizer and irrigation supply to the cane fields (Kojima and Johnson 2005).

Sugar cane must be processed within 24–72 h after being harvested. Sugar is first extracted by crushing the stalks, to release the juice (Fig. 1.5). Calcium hydroxide is then added to precipitate the fiber and the sludge, and the mixture is then filtered. The filtrate solution is evaporated to concentrate and crystallize the sugar. The sugar is removed by centrifugation.

The sugar which is not crystallized and the accompanying salts are concentrated to form a syrup called molasses. These are used to produce ethanol (Kojima and Johnson 2005). To achieve the optimum fermentation efficiency of yeast *Saccharomyces cerevisiae*, the sugar content in the molasses has to be adjusted in the range of 14–18%wt. The typical temperature of the fermentation process is about 33–35 °C, while cell density is about 8–17% (v/v). Cell recycle system can be used to concentrate yeasts and recycle them into the process, obtaining high cell densities, which shorten fermentations to 6–10 h (Wyman 2004). Fermentation is interrupted at concentration of approximately 10% (v/v) ethanol. Fermentation reaction is the following:



The next step is represented by distillation and rectification. An azeotropic solution of 95% (v/v) ethanol is obtained. Further concentration to absolute ethanol is finally achieved by molecular sieves or azeotropic distillation (using benzene or cyclohexane) (Chiamonti 2007).

1.4.2 Bioethanol Production from Starch

As reported in Table 1.3, grains (corn, wheat, or barley) mainly provide starch. This is made up of long chains of glucose units. The amylose structure contains 1000 monomeric units, while the amylopectin structure contains 1000–6000 units. Starch is the most utilized for ethanol production in North America and Europe. To produce ethanol it is necessary to hydrolyze the starch into monomers. The hydrolytic reaction is catalyzed by glucoamylase enzyme. D-glucose, which is an isomer of glucose, is obtained as final hydrolysis product. Enzymatic hydrolysis is then followed by fermentation, distillation, and dehydration to yield anhydrous ethanol (Kumar et al. 2010).

There are two distinct methods for processing corn: wet milling and dry milling. Dry mills are usually smaller in size and are built primarily to produce only ethanol. Wet mill facilities also produce a list of high-valued co-products such as high-fructose corn syrup, corn oil, and corn gluten.

Corn dry-milling process is carried out in five steps (Vohra et al. 2014):

- (i) Biomass handling (milling)
- (ii) Liquefaction
- (iii) Hydrolysis (saccharification)
- (iv) Fermentation
- (v) Distillation and recovery

In dry-grind process, the corns are milled to a powder and heated with water at 85°C (Kojima and Johnson 2005). Then hot water and alpha-amylase enzymes are added and the mixture is heated at 110–150 °C for an hour. This causes the liquefaction of starch. When liquefaction is completed, the mixture is cooled down and glucoamylases are added to produce dextrose. In dry-grind milling plants, often the glucoamylases are directly added into the fermentor. The process is known as “simultaneous saccharification and fermentation” (SSF) (Fig. 1.6).

In the fermentation process, yeasts convert glucose into ethanol and carbon dioxide. The process is completed in about 40–50 h. During fermentation, the mash is continuously mixed and it is cooled down. The beer obtained from fermentation is transferred to the distillation columns where ethanol is separated from the stillage (Singh et al. 2001). The stillage contains protein, oil, and fiber and are dried to obtain dried grains with solubles (DDGS) or just distillers dried grains (DDG). DDGS contain the process syrup combined with the solids, while DDG don't contain it.

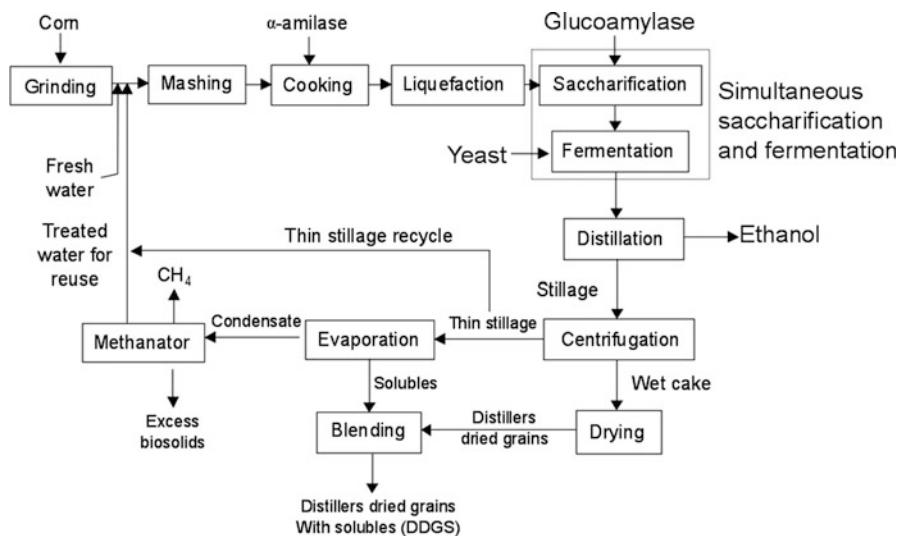


Fig. 1.6 Corn dry milling process flow diagram (Vohra et al. 2014)

In wet milling the shelled corns pass through mechanical cleaners designed to remove unwanted material, such as pieces of cobs, sticks, husks, meal, and stones. The cleaned corns are then fed into “steep” tanks, where they are soaked in dilute sulfuric acid and remain for 24 to 48 h at a temperature of about 52°C. Steeping softens the kernel and helps to break down the protein holding the starch particles. Generally, water drained from the steep tank, called “light steep water” contains about 6% of the original dry weight of the grains and is discharged to multiple-effect evaporators. The solids from steep water are rich in protein and are concentrated to 30–55% solids. The resulting steeping liquor can be sold as animal feed (May 1994) (Fig. 1.7).

The germ is removed from the steeped corn in the degerminating mills, which break the kernel to free the germ, the starch, and the gluten. The germ is separated in liquid cyclones from the mixture of fiber, starch, and gluten. It is then washed, dewatered, dried, and further processed to extract corn oil (Bothast and Schlicher 2005).

The starch and gluten are separated from the fiber by further washing, grinding, and screening operations. The solids and the fiber are used as a feed. The starch is separated from the gluten by centrifugation (May 1994; Bothast and Schlicher 2005). Once the pure starch slurry is obtained, the wet-mill process is similar to that of dry milling. First, the pH of the slurry is adjusted to 5.8–6.2 with calcium hydroxide, and then alpha-amylase is added to convert the starch into soluble short-chain dextrins (liquefaction). Calcium is often added (20–100 ppm) to enhance enzyme stability.

The slurry from the liquefaction stage is mixed with heat-sterilized steep water and sent for saccharification. The steep water provides both the fermentation

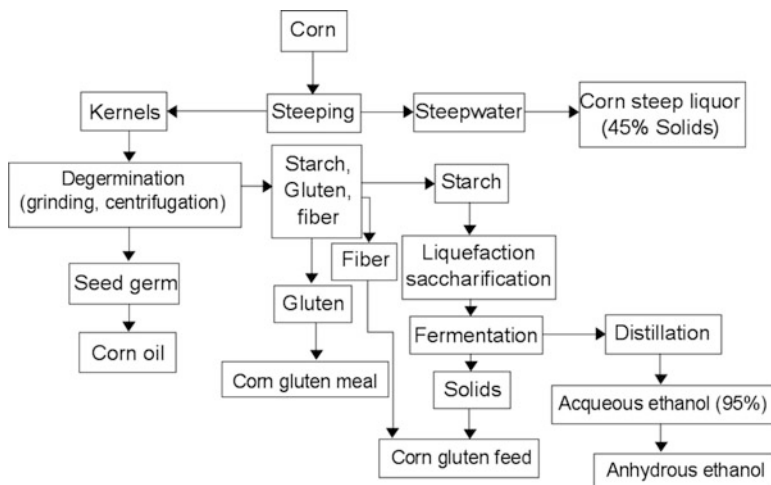


Fig. 1.7 Corn wet milling process flow diagram (Vohra et al. 2014)

nutrients and pH adjustment for saccharification, in which the glucoamylase converts the dextrins to glucose at a pH of 4.5 and a temperature of 65 °C. Then *S. cerevisiae* is added to ferment the sugars to ethanol and CO₂. The total fermentation time varies from 20 to 60 h. The final product from a continuous process will have an ethanol content of 8–10%v (Kojima and Johnson 2005; Bothast and Schlicher 2005).

1.4.3 Bioethanol Production From Lignocellulosic Feedstock

Bioethanol produced from lignocellulosic materials is commonly known as second-generation bioethanol. There have been huge research efforts in developing economically feasible advanced technologies for ethanol production; however, some challenges are still remaining (Cheng and Timilsina 2011). Chemical composition of lignocellulosic materials is the key factor affecting efficiency of biofuel production. Cellulose and hemicellulose are more present in hardwoods (78.8%) than softwoods (70.3%), while lignin is more present in softwoods (29.2%) than hardwoods (21.7%) (Balat 2011). According to (Vohra et al. 2014), the technologies for the conversion of lignocellulosic feedstocks to ethanol can be grouped into two broad macrocategories:

- The sugar platform (biochemical conversion)
- The syngas platform (thermochemical conversion)

The sugar platform uses enzymes to convert lignocellulosic biomass materials into sugars, while the syngas platform gasifies biomass and converts syngas into ethanol (Datta et al. 2011).

The biochemical platform consists of three main processes (Cotana et al. 2015; Barbanera et al. 2018; Buratti et al. 2015, 2018; Cavalaglio et al. 2016):

- Pretreatment
- Enzymatic hydrolysis
- Fermentation

1.4.3.1 Pretreatment

The pretreatment process significantly affects all the downstream processes and ultimately influences the overall biofuel yield and cost.

Pretreatment step can be performed through biological, physical, and chemical processes or a combination of them. Chemical methods use dilute acids (such as sulfuric or hydrochloric acid), alkalis (such as calcium hydroxide), and liquid ammonia (the ammonia fiber explosion pretreatment), while a physical method is represented by steam explosion (Ruane et al. 2010).

Pretreatment with dilute acid and intermediate temperatures is generally considered quite cost-effective. It loosens the cell wall matrix through degradation of hemicelluloses. Lignin is unaffected by this process. Accessibility to cellulose microfibrils is increased to provide a higher yield of sugars for fermentation. Acid treatment will result in other high-value products like furfural, hydroxyl-methyl furfural (HMF), phenolics, aldehydes, and aliphatic compounds. These products have to be removed before using the residues for further biochemical treatments. Acid pretreatment processes have to be followed by neutralization and detoxification (Kurian et al. 2013).

Steam explosion is the physical treatment where the lignocellulosic biomass is subjected to high pressures and temperatures for short duration, followed by the rapid decrease to atmospheric pressure, which will break the polymeric bonds in the substrate. Temperatures can range between 180 and 250 °C, pressures can range between 1 and 5 MPa (Jacquet et al. 2011).

Steam explosion has the following advantages:

- Lower capital investment
- Significantly lower environmental impact
- More potential for energy efficiency
- Less hazardous process conditions
- Complete sugar recovery

To compare steam explosion conditions, the severity factor has to be taken into account, defined as (Li et al. 2005)

$$S_0 = \log\{\exp[(T - 100)/14.75]t\} \quad (1.2)$$

where T is the temperature (°C) and t is the duration of treatment (min).

Steam explosion is considered the most cost-effective option for hardwood and agriculture residues, while it is less effective for softwood. Acid catalysis can be used

also within the steam explosion treatment and is found to reduce the temperature and the retention time. Another advantage is that complete hydrolysis of hemicellulose can be achieved (Mood et al. 2013).

1.4.3.2 Hydrolysis

During the hydrolysis, polysaccharides are broken down to simple sugars. Two examples of hydrolysis methods of cellulose into glucose are (Lynd et al. 2002):

1. Concentrated acid (H_2SO_4 30–70%, 40 °C, a few hours to achieve >90% glucose yields)
2. Enzymatic hydrolysis (cellulase mixture, 50 °C several days to reach 75–95% glucose yields)

The current trend is to use enzymatic hydrolysis to avoid costly recovery and wastewater treatment requirements, resulting from the use of acid hydrolysis. Enzymatic hydrolysis is attractive because it produces better yields than acid-catalyzed hydrolysis and enzyme producers have recently reduced their cost using biotechnology (Ruane et al. 2010). The conversion of cellulose and hemicellulose is catalyzed by cellulase and hemicellulase enzymes, respectively.

1.4.3.3 Fermentation

The ability to use the hemicellulose component in biomass feedstock is critical for any bio-ethanol plant. *Saccharomyces cerevisiae* and *Zymomonas mobilis*, the commonly employed organisms in alcohol fermentation, are not able to ferment hemicellulose-derived pentose (C5) sugars. There are organisms that can ferment C5 sugars (e.g., *Pichia stipitis*, *Pachysolen tannophilus*, *Candida shehatae*), but their efficiencies are low. They also need microaerophilic conditions. This implies that for more than 20 years research activities have focused on the development of improved microorganisms for the fermentation of pentose sugars (Hahn-hägerdal et al. 2007). Besides this, currently there are not known natural organisms that have the ability to convert both these C6 and C5 sugars at high yields. While pentose fermentation has been achieved on ideal substrates, (i.e., laboratory preparations of sugars designed to imitate a perfectly pretreated feedstock), significant work remains to apply this to real lignocellulosic feedstocks (Sims et al. 2008). Lignocellulosic biomass conversion into bioethanol flow diagram is shown in Fig. 1.8.

A typical process for making cellulosic ethanol starts with pretreatment and separation of the insolubles. The insoluble fraction is then hydrolyzed with cellulase and glycosidases to release glucose, which is fermented to produce ethanol. The residual insoluble material, mostly lignin, is burned to generate energy (Ruane et al. 2010). If the fermentation process is performed after the hydrolysis, this is called separate hydrolysis and fermentation (SHF). The fermentation process produces wastewaters which can be used to recover a nutrient-rich microbial cell mass (Kurian et al. 2013). Pentose fermentation, when it is carried out, is accomplished in an independent unit. The advantage of SHF is the ability to carry out each step under

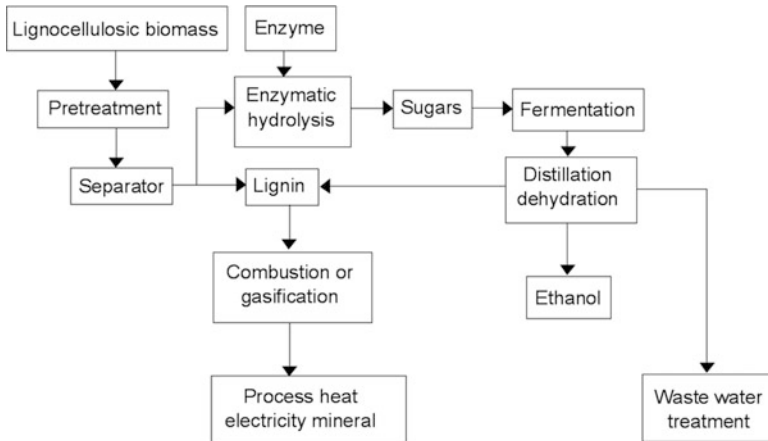


Fig. 1.8 Lignocellulosic biomass conversion into bioethanol process flow diagram (Vohra et al. 2014)

optimal conditions, i.e., enzymatic hydrolysis at 45–50 °C and fermentation at about 35 °C (Cardona and Sanchez 2007; Kurian et al. 2013). Hydrolysis and fermentation can also be performed through integrated techniques, such as simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP) (Vohra et al. 2014).

1.4.3.4 Bioethanol Production Through Syngas Fermentation

Syngas conversion using microbial catalysts offers three main advantages:

- It requires significantly lower temperature and pressure conditions (usually atmospheric conditions).
- It is less susceptible to varying feed gas compositions.
- Chemical catalysts are more susceptible to poisoning, compared to microbial processes (Köpke et al. 2011).

After biomass gasification has been performed, cleaned gas is cooled to the normal ambient temperature and stored at a high pressure. The gas is then fed into an ethanol conversion chamber, where microbes ferment it into ethanol and acetic acid. After fermentation is completed, the liquid is distilled to separate ethanol from other products. Then ethanol is dehydrated (Dwivedi et al. 2009); see Fig. 1.9.

A large number of bacterial strains have been isolated that have the ability to ferment producer gas (composed by CO, CO₂, and H₂) to ethanol, acetic acid, and other useful liquid products; see, for example, *Clostridium ljungdahlii* (Henstra et al. 2007), *Butyribacterium methylotrophicum*, and *Clostridium autoethanogenum* (Abubackar et al. 2011).

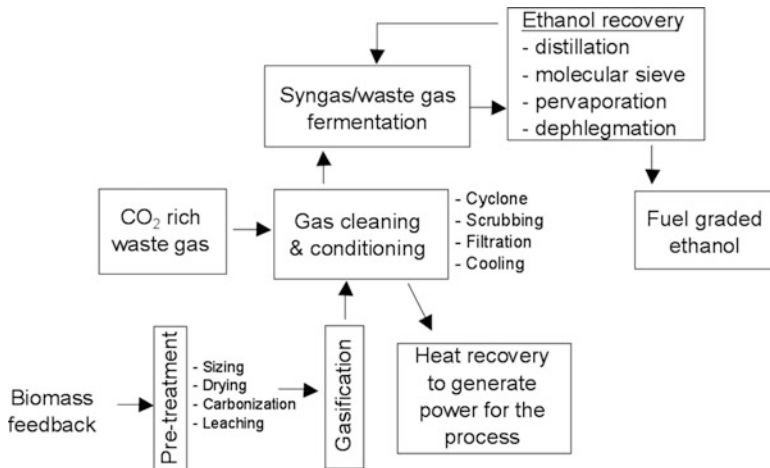


Fig. 1.9 Microbial fermentation of syngas (Vohra et al. 2014)

Producer gas fermentation is a technology which has not yet reached the market, because of low productivity of the bioreactor. This is due to several factors, such as (Ungerma and Heindel 2007):

- Low cell density
- Lack of regulation of metabolic pathways to yield only the desired product
- Inhibition of the biological catalysts by products and substrates
- Low gas–liquid mass transfer

At mild temperatures, CO and H₂ have aqueous solubilities of 60% and 4%, with respect to oxygen, on a mass basis. This results in low concentration gradients and, hence, low mass transfer rates. Higher mass transfer rates can be achieved using:

- An agitator system
- Increasing the operating pressure
- Producing micro-bubble dispersions (bubbles with diameters of about 50–100 μm have been used to provide a large gas transport area at low power consumption (Lewis et al. 2006))

1.5 BTL (FT-Diesel, Methanol and DME)

1.5.1 Introduction

The term “BTL” is applied to a liquid fuel obtained through thermo-chemical processes, such as pyrolysis and gasification, applied to biomass.

While large-scale coal-to-liquid (CTL) and gas-to-liquid (GTL) processes have been commercialized for decades (e.g., Sasol and Shell plants) (Dimitriou et al. 2018), this is not the case of BTL processes. Only a few plants have been built to date on pilot and demonstration scale:

- In the late nineties, Choren started operating a 1MWth BTL plant in Freiberg, Germany, which is not working anymore (Dimitriou et al. 2018).
- NSE Biofuels Oy operated a 12MWth (656 t/yr of fuels) BTL demonstration plant in Finland from 2009 to 2011, based on a circulating fluidized bed (CFB) gasifier designed by Foster Wheeler (Neste Oil Corporation n.d.).
- In 2010, five French partners and Uhde launched BioTfuel with two pilot plants currently on operation in France: a biomass torrefaction unit in Venette and an entrained flow gasification and Fischer-Tropsch (FT) synthesis plant near Dunkirk (Dimitriou et al. 2018).
- The Karlsruhe Institute of Technology (KIT) bioliq pilot plant with a capacity of 1 t/day has been in operation since 2014 using a process similar to the Topsoe TIGAS process.

Biomass-to-liquid (BTL) is a multistep process which consists of the following phases:

1. Reception, storage, handling, and preparation
2. Biomass gasification
3. Gas cleaning and conditioning
4. Fuel synthesis

1.5.2 Reception, Storage, Handling, and Preparation

Biomass, which is mainly transported by road, after storage is conveyed to a magnetic separator (to separate iron parts and impurities) and then screened to keep particle sizes within appropriate limits.

Biomass drying can be performed either by hot air (rotary dryer) or steam (superheated steam dryer). Air rotary dryers are the most common (WA A 1998), while superheated steam dryers (SSD) are less common but are safer with respect to fire hazards. Fuel synthesis processes (such as FT synthesis) generate significant amounts of steam, which can be reused to dry biomass (at the temperature of 200 °C and pressure of 12 bar) (Dimitriou et al. 2018).

A grinder (hammer mill) has to be placed after the dryer in case the fuel will be used in an entrained flow gasifier, to reduce the wood chips size to 1mm (Van der Drift et al. 2004; Swanson et al. 2010). If a circulating fluidized bed gasifier is used, this is capable of handling a wider variety of biomass particle sizes (Bridgwater and Maniatis 2014), so no grinding would be required.

1.5.3 Biomass Gasification

The two gasification technologies best suited for large-scale BTL plants are the circulating fluidized bed (CFB) and the entrained flow (EF) gasification (Swanson et al. 2010; Bridgwater and Maniatis 2014; The Royal Society 2008; Boerrigter 2006; The German Energy Agency 2006). For circulating fluidized bed gasifiers, operating temperature varies between 700 and 1100 °C. EF gasifiers can operate at much higher gasification temperatures (about 1200–1400 °C); this results in higher carbon conversion, very low tar and methane content, and thus lower gas cleaning requirements (Van der Drift et al. 2004; Swanson et al. 2010; Boerrigter 2006). EF gasification has the advantage that extensive experience is available from coal entrained flow gasification plants (e.g., 2000 t/d coal-fired Shell gasifier in Buggenum, Netherlands) (Hofbauer et al. 2009; Dimitriou et al. 2018). For both reactors best operating conditions are oxygen-blown and pressurized (using CO₂) (Dimitriou et al. 2018). For example, oxygen at 95% purity and steam can be fed into the gasifiers operating at a pressure of 28 bar and temperatures of 870 °C for the CFB and 1400 °C for the EF gasifier, respectively (Swanson et al. 2010; Dimitriou et al. 2018).

Generally the entrained flow reactor produces a syngas with higher concentration of hydrogen and carbon monoxide, as a result of reforming of light hydrocarbons. The CFB gasifier, on the other hand, produces more tar and a significant amount of methane and other light hydrocarbons (Table 1.5).

Table 1.5 Producer gas composition, depending on the reactor (Dimitriou et al. 2018)

	CFB gasifier	EF gasifier
P (bar)	28	28
T (°C)	870	1400
Oxygen (kg/kg dry feed)	0.32	0.6
Steam (kg/kg dry feed)	0.17	0.15
Gas composition (vol% wet basis [dry basis])		
H ₂ O	12.6 [0]	25 [0]
H ₂	28.3 [32.4]	25.9 [34.5]
CO	26 [29.8]	37.1 [49.5]
CO ₂	21.2 [24.2]	10.8 [14.4]
CH ₄	10.5 [12]	0 [0]
C ₂ +	0.52 [0.6]	0 [0]
Ar	0.27 [0.3]	0.42 [0.55]
N ₂	0.56 [0.62]	0.75 [0.99]
NH ₃	0.005 [5.8 × 10 ⁻³]	0 [0]
H ₂ S	0.02 [0.024]	0.017 [0.023]
HCl	0.01 [0.013]	0.009 [0.013]
HCN	5 × 10 ⁻⁴ [6 × 10 ⁻⁴]	0 [0]

1.5.4 Gas Cleaning

Gas cleaning is the biggest challenge to the development of a successful BTL plant. The impurities in syngas need to be reduced to the level demanded by the catalytic fuel synthesis processes.

For CFB gasification, a cyclone can be used for particulates separation, and then syngas should pass through a tar cracker, where tars are destroyed at 875 °C by addition of oxygen and steam. The tar-free syngas is then cooled down to 280 °C using a heat exchanger. The cooled syngas passes through a bag filter (Hofbauer et al. 2009) and then is fed to the Rectisol unit, where CO₂ and sulfur compounds are removed (Hofbauer et al. 2009).

For the EF gasification concept, if the H₂/CO molar ratio of the dust-free syngas produced by the entrained flow gasifier is lower than the required ratio (H₂/CO = 2) for FT and methanol synthesis, a water-gas-shift (WGS) reactor should be added before the Rectisol process. In that way the carbon dioxide produced in the WGS unit can be removed soon after in the Rectisol unit. So the dust-free syngas is fed to a direct water quench where it is cooled to the operating temperature of the WGS reactor (200 °C) (Swanson et al. 2010). The cooled syngas then passes through a bag filter to remove particulates and then enters the Rectisol unit.

1.5.5 Fuel Synthesis

After the Rectisol unit, liquid fuels can be produced from syngas using:

- FT synthesis
- Methanol synthesis followed by the MTG process
- The TIGAS process

These three processes are currently the most reliable syngas conversion technologies for transport fuel production available on the market. FT synthesis has already been used in large-scale coal-to-liquid (CTL) and gas-to-liquid (GTL) plants worldwide (Mangena 2012; Fleisch et al. 2002). Both the MTG and the TIGAS technologies have been successfully proven at demonstration scale (Fürnsinn 2007; Topp-Jorgensen 1988).

1.5.5.1 Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis is a process for catalytically converting syngas to mainly hydrocarbon products of different chain lengths (typically from C1 to C100). Among the most widely known fuel synthesis plants in the world are:

- The CTL Fischer-Tropsch plants operated by Sasol in South Africa, which is the world's largest CTL production facility producing 27% of South Africa's total liquid fuel production (Mangena 2012).

- The Pearl GTL is the largest implementation of FT synthesis, located in Qatar and owned by Shell (Fleisch et al. 2002).
- CHOREN's has realized a 1MWth Carbo-V gasifier coupled to a Fischer-Tropsch reactor in 2002 (Dimitriou et al. 2018).

If cobalt-based catalyst is used, the FT synthesis takes place at 230 °C and 25 bar (Fleisch et al. 2002). The product distribution can be estimated using the Anderson-Schulz-Flory (ASF) model with an alpha value of 0.85 which favors the production of middle distillates (Swanson et al. 2010; Fürnsinn 2007; Taschler 2009). A product distribution of 60% diesel, 25% gasoline, and 25% kerosene can be achieved after the hydrocracking unit, as reported for the Shell Middle Distillate Synthesis (SMDS) process (Eilers et al. 1990).

1.5.5.2 Methanol-to-Gasoline (MTG) Synthesis

In the methanol-to-gasoline (MTG) process, the first step is represented by methanol synthesis from syngas at 50 bar and 250 °C (LeBlanc et al. 1994; Lee 1990). The produced methanol is vaporized, before it enters a dehydration reactor, where a mixture of DME, methanol, and water is produced at 404 °C. The effluent from the DME reactor is combined with the recycled gas from the product separator and enters the MTG reactor, where it is converted at 415 °C and 21.2 bar to mainly hydrocarbons and water over zeolite catalysts (ZSM-5) (Maiden 1988). The gasoline fraction in the product stream is usually about 36 wt% of the methanol and DME input (Yurchak 1988). The hot reactor effluent is cooled by heat exchange with the gas recycled from the vapor-liquid separator. It is then further cooled to about 200 °C before it passes to the vapor-liquid separator, where gas, liquid gasoline, and water are the outputs.

The MTG process was developed by Mobil scientists in the 1970s (Keil 1999). A Mobil MTG plant was operated in Motunui, New Zealand, from 1985 to 1997 and produced 14,500 bbl/d of gasoline. The plant was designed to meet one-third of New Zealand's demand for transport fuels (Maiden 1988). The fuel was composed mainly of isoparaffins and aromatics with low benzene content and essentially zero sulfur (Spath and Dayton 2003).

The first coal-to-gasoline MTG plant, utilizing the second-generation MTG technology, was constructed by Jincheng Anthracite Mining Group (JAMG) in China (Dimitriou et al. 2018). The plant started up in 2009 and its current capacity is 2500 bpd (Dimitriou et al. 2018).

1.5.5.3 Topsoe Integrated Gasoline Synthesis (TIGAS)

The main principle of the TIGAS process is the incorporation of the methanol synthesis and the DME synthesis into a single process. It was developed by Haldor Topsoe to reduce investment costs and subsequently production costs of gasoline (Topp-Jorgensen 1988). The process has been demonstrated in Houston, Texas, using natural gas as feed to the process. The plant capacity was 1 t per day gasoline. The plant started working in early 1984 and terminated in January 1987 after

10,000 h of operation (Topp-Jorgensen 1988). The bioliq Process developed by Karlsruhe Institute of Technology (KIT), with a capacity of 1 t/day, is a similar process. It is in operation since 2014 and incorporates the following processing steps: decentralized fast pyrolysis to produce a pyrolysis bio-oil/char slurry, high-pressure entrained flow gasification of the pyrolysis slurry, hot gas cleaning, DME synthesis, and gasoline synthesis (Dimitriou et al. 2018).

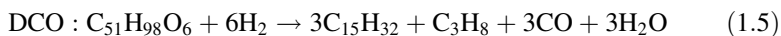
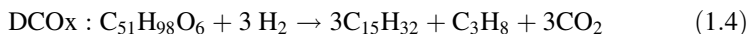
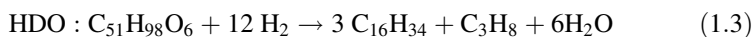
The DME synthesis reactor operates at 250 °C (Larson et al. 2009). The gasoline synthesis reactor is quite similar to that of the MGT process. Then the gasoline product is separated from gas and water in a vapor-liquid separator.

1.6 Hydrotreated Vegetable Oils (HVO)

Saturating the double bonds present in a molecule through catalytic addition of hydrogen at certain temperature and pressure is known as “hydrogenation” (Hughes 1953). In the process known as “hydrotreatment” hydrogen, alongside a catalyst, is added after hydrogenation. After saturation is achieved, more hydrogen addition causes the breaking of the glycerol compound, forming propane and a chain of FFA. The carboxylic acid group of the FFA must be removed to form straight-chain alkanes. This can be performed through three ways:

- The hydrodeoxygenation (HDO) route, in which it reacts with hydrogen to produce a hydrocarbon with the same number of carbon atoms as the fatty acid chain and two moles of water
- The decarboxylation (DCOX) pathway, which yields a hydrocarbon with one carbon atom less than the fatty acid chain and a mole of CO₂
- The decarbonylation (DCO) route, which also produces a hydrocarbon with one carbon atom less, as well as a mole of CO and water

The hydrodeoxygenation and hydrodecarboxylation reactions shown in Figure 1.10 can be exemplified using a saturated molecule (palmitic triglyceride) in the next set of equations (Jeczmiónek and Porzycka-Semczuk 2014):



The HDO reaction consumes 12 mol of H₂ per mole of required triglyceride, while DCOx reaction consumes 3 moles of H₂ and DCO reaction consumes 6 moles of H₂. An additional mole of H₂ is required for each double bond that is present in the vegetable oil to grant saturation. The more saturated the feedstock is, the more it

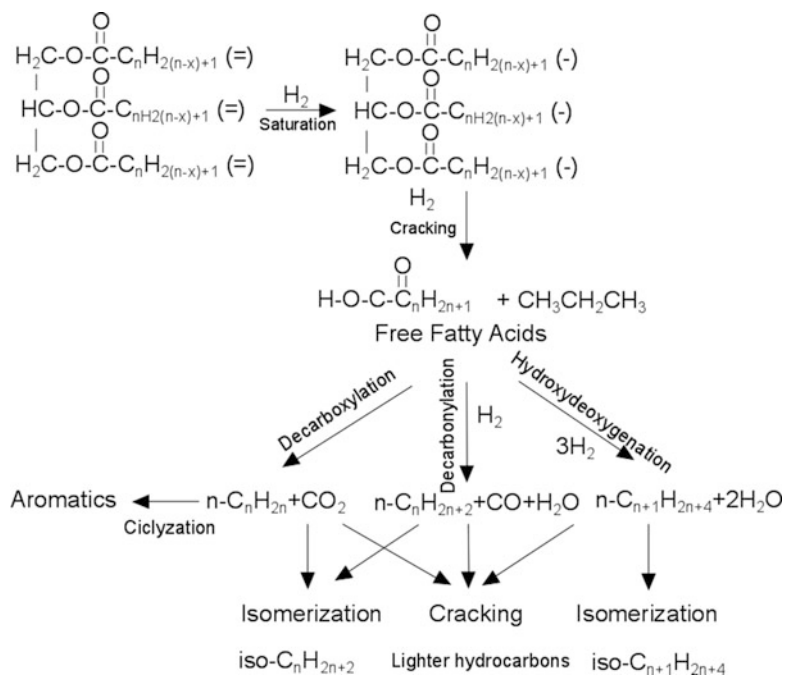
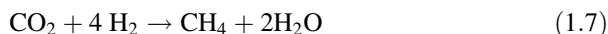


Fig. 1.10 Reactions happening during catalytic hydrotreatment (Vásquez et al. 2017); n , odd number; x, y, z , number of double bonds; $=$, double bonds; $-$, single bond; HDO, exothermic; DCOx, endothermic

is desirable, because less hydrogen will be needed during hydrogenation. The index determining unsaturation of fatty acids is known as iodine value (IV).

It has to be also considered that the CO and CO₂ formed during hydrodecarboxylation reactions may be converted into CH₄ through a methanation reaction, and further addition of hydrogen would be necessary, as shown in equations (1.6) and (1.7) (Melero et al. 2012; Kaewmeesri et al. 2015):



This implies that globally hydrodecarboxylation route will demand three more molecules of hydrogen than the hydrodeoxygenation pathway.

Depending of the composition of the final n -alkanes produced though the hydrotreatment process, they need to be subjected to either isomerization, cracking, or cyclization, to improve their combustion properties and obtain isoalkanes, lighter hydrocarbons, and aromatics, respectively (Veriansyah et al. 2012; Kiatkittipong et al. 2013).

During hydrotreatment, there are some variables that influence the process and the final composition of the product, including:

- Reaction conditions
- Type of catalyst used
- Selected feedstock

Dealing with reaction temperature, DCO and DCOX are more dominant over higher temperatures and moderate acidic catalyst than HDO reaction.

Two types of catalyst can be used for the hydrotreatment:

- Conventional bimetallic sulfide catalysts, such as NiMoS₂, CoMoS₂, and NiWS₂ supported on Al₂O₃
- Monometallic catalysts, in particular Ni, Pd, Pt, and Rh (Morgan et al. 2012; Rogers and Zheng 2016)

Nickel- and palladium-based catalysts are the most commonly used catalysts. Metal catalysts supported on activated carbon have been also tested for upgrading vegetable oils into hydrocarbon jet biofuels (Silva et al. 2016). Zeolite catalysts have been also studied for the hydrotreatment of vegetable oils (Zhao et al. 2015).

The process shown in Figure 1.11 consists mainly in a pretreatment of the raw material, a deoxygenation, a hydrocracking/isomerization, and a distillation (Hilbers et al. 2015). As it can be seen from Figure 1.11, the hydrotreating process is interesting for the production of both biodiesel and bio-jet fuel.

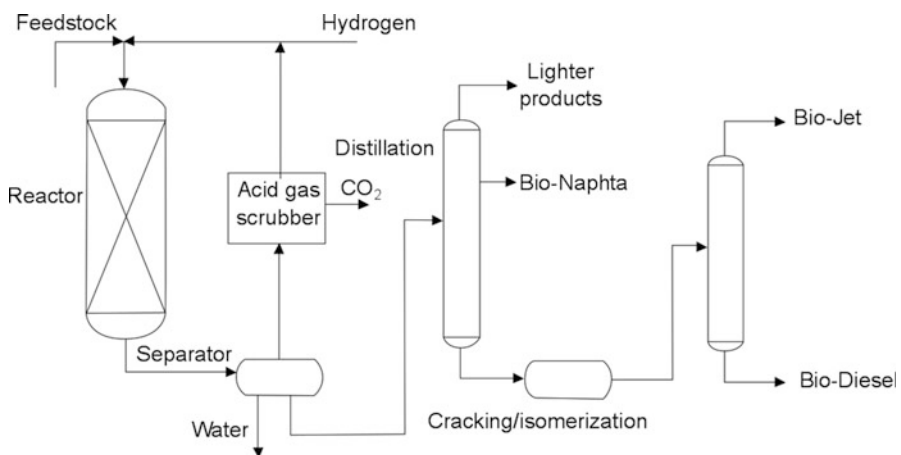


Fig. 1.11 Hydrotreatment of vegetable oils process diagram (Vásquez et al. 2017)

1.6.1 HVO Biofuel Plants

Neste Corporation is the leading company on HVO production, accounting for an annual production volume of more than 2 million tons of biofuel. Based in Finland, the company has two renewable refineries in Porvoo and two more abroad (i.e., in the Netherlands and in Singapore) (Vásquez et al. 2017). They developed the NExBTL technology, and currently, they process 10 types of raw materials including animal fats (food industry waste), fish fat (fish processing waste), vegetable oils, used cooking oil, and technical corn oil, though the focus is on waste and residue raw materials which account for an 80% of the feedstock.

Main competitor of NExBTL technology is the Ecofining Process, developed by the Honeywell UOP company, jointly with the Eni S.p.A (GREENEA 2015).

Some other technologies for the conversion of lipids through hydrotreatment are (Vásquez et al. 2017):

- The Vegan Technology marketed by the Axens Group, a French company
- Bio-Synfining process, patented by Syntroleum Corporation and bought by the Renewable Energy Group (United States) in 2014 (a plant with a capacity of 75 million gallons per year is operative)
- The UPM BioVerno technology, which converts crude tall oil into green diesel, developed by UPM Biofuels Company in Finland
- The Hydroflex technology created by the Haldor Topsøe group in Denmark, allowing its implementation as both stand-alone or co-processing unit (Vásquez et al. 2017)

1.6.2 HVO Jet Biofuel Plants

Most commercial applications of the hydrotreating process are optimized to produce green diesel; however, multiple agreements between airlines and refineries have boosted also jet biofuel production projects:

- SG Preston, in the United States, has signed a ten-year agreement with JetBlue Airways to deliver more than 33 million gallons of HEFA (hydroprocessed esters and fatty acids) jet per year.
- AltAir fuels have a dedicated capacity to produce jet biofuel to provide United Airlines 15 million gallons of sustainable biofuel over a three-year period contract. AltAir will also provide KLM Royal Dutch Airlines with sustainable jet fuel.
- Petrixo Oil & Gas is expected to be the most massive jet biofuel project, producing over 500,000 metric tons per year of jet biofuel at its new refinery to be built in Fujairah, United Arab Emirates (BiofuelsDigets 2017).

Table 1.6 Biofuel yields and costs for different feedstock and technologies (Festel et al. 2014)

Biofuel	Raw material	Yield (l/t)	Costs (€Cent/l) referred to 2015
Ethanol	Maize	400	105.85
Ethanol	Wheat	375	136.40
Ethanol	Lignocellulosic waste	250	157.34
Biodiesel	Rapeseed oil	1100	117.49
Biodiesel	Palm oil	1100	70.00
Biodiesel	Waste oil	1100	61.78
HVO	Palm oil	1100	216.18
BTL	Wood	158	827.95

1.7 Biofuel Yields and Costs

Table 1.6 shows the yields of ethanol, biodiesel, HVO, and BTL. Biodiesel and HVO have very higher yields. Bioethanol has less than half of the mass yield of biodiesel, while BTL has 14% of the yield of biodiesel.

Biofuels' costs have been calculated through the methodology presented in (Festel et al. 2014). This is based on the development of scenarios on future raw material prices and on the modeling of production costs. The cost of raw materials is obviously influenced by the price of oil (for the results shown in Table 1.6, a price of oil of 50 € per barrel is supposed).

If we consider that according to (Festel et al. 2014) a price of oil equal to 50 € per barrel corresponds to a cost of oil equal to 36.45 €/l, we see that no biofuel can be produced at competitive cost compared to fossil fuel. The biofuel with lower cost is biodiesel especially that produced from waste oil.

1.8 Biofuel Properties and Combustion Performance

Biofuels properties are shown in Table 1.7.

Table 1.7 shows that gasoline, fossil diesel, and HVO have very high heating values, compared to bioethanol and biodiesel. The main issue with use of ethanol comes from its lower energy density; in fact it contains only around two-thirds of the energy of a similar volume of gasoline (Gautam and Martin II 2000). This is not an issue during normal driving; however, it will result in reduced vehicle range and a lower peak power of the engine when the accelerator is fully pressed. An advantage is represented by the fact that it has higher octane rating of ethanol as compared to gasoline. This can allow higher compression ratio engines to be used (Bergthorson and Thomson 2015) increasing in this way the fuel efficiency. When blended with hydrocarbon fuels, ethanol acts as a sink of reactive species (OH radicals) that disrupts the chain branching of the hydrocarbon fuel under low-temperature chemistry conditions and slows ignition of the blend (Foong et al. 2014). It is, however, high-temperature flame chemistry which controls the combustion efficiency and

Table 1.7 Biofuels properties

Property	Fossil diesel (EN590)	Biodiesel (EN 14214)	HVO	Bioethanol	Gasoline
Density (kg/m ³ at 15°C)	820–845 (Vásquez et al. 2017)	860–900 (Vásquez et al. 2017)	775–785 (Vásquez et al. 2017)	785 (Ku and Tu 2005)	720–780 (Christensen et al. 2011)
Viscosity (mm ² /s at 40°C)	2–4.5 (Vásquez et al. 2017)	3.5–5.0 (Vásquez et al. 2017)	2.9–3.5 (Vásquez et al. 2017)	1.1 (Ku and Tu 2005)	0.37–0.44 (Christensen et al. 2011)
Heating value (MJ/kg)	43 (Vásquez et al. 2017)	38 (Vásquez et al. 2017)	44 (Vásquez et al. 2017)	26.87 (Agarwal 2007)	44 (Al-Hasan 2003)
Cetane number	51> (Vásquez et al. 2017)	51> (Vásquez et al. 2017)	84–99 (Vásquez et al. 2017)	6 (Yilmaz 2012)	n.a.
Sulfur content (mg/kg)	<10 (Vásquez et al. 2017)	<1 (Vásquez et al. 2017)	0 (Vásquez et al. 2017)	0 (Agarwal 2007)	7 (Rodríguez-Antón et al. 2015)
Oxygen content (wt%)	0 (Vásquez et al. 2017)	11 (Vásquez et al. 2017)	0 (Vásquez et al. 2017)]	5 (Rodríguez-Antón et al. 2015)	2.7 (Rodríguez-Antón et al. 2015)

*Calculated

pollutant emissions in SI engines. After ignition by the spark, a turbulent premixed flame propagates through the premixed fuel–air charge in the engine, rapidly converting the fuel into combustion products and producing the thermal energy and pressure that drive the engine. A recent study observing flames in optically accessible engines has shown that ethanol flames propagate faster than butanol, gasoline, and iso-octane (Aleiferis et al. 2013). Recent papers still do not produce consistent trends in relative NO_x potential of gasoline–alcohol blends (Karavalakis et al. 2014; Canakci et al. 2013; Gravalos et al. 2013; Balki et al. 2014), while agreement is growing on the risk of a potential increase in oxygenated emissions, such as formaldehyde, acetaldehyde, and ketones (Agarwal 2007; Lynd et al. 1991; Kohse-Höinghaus et al. 2010; Saxena and Williams 2007).

Dealing with biodiesel, when compared to diesel, it has a 9% lower volumetric energy content, due to its oxygen content (Agarwal 2007; Lapuerta et al. 2008). At high-temperatures, the reactivity of long-chain esters is nearly indistinguishable for saturated and unsaturated esters (Wang et al. 2013), while the unsaturated esters (with double bonds) have generally increased low-temperature ignition delay times and reduced cetane numbers (Westbrook 2013; Westbrook et al. 2013). Biodiesels have the positive aspect of reducing engine deposits and coking, compared to petroleum-derived fuels (Graboski and McCormick 1998; Xue et al. 2011). NO_x emissions have been observed to increase for biodiesel compared to petro-diesel for many engine tests (Lapuerta et al. 2008; Graboski and McCormick 1998; Xue et al. 2011; Coniglio et al. 2013; Lai et al. 2011; Sun et al. 2010; Giakoumis et al. 2012; Palash et al. 2013; Varatharajan and Cheralathan 2012; Szybist et al. 2007; Hoekman

and Robbins 2012; Mueller et al. 2009; Szybist et al. 2005; Rajasekar et al. 2010), while others have shown no increase or even a decrease (Coniglio et al. 2013).

Renewable diesel fuel derived from either hydrotreating vegetable oils is more compatible with existing engine technology than first-generation biodiesels, thus leading to improved engine performance (Knothe 2010; Gill et al. 2011). These renewable fuels have effectively equivalent energy densities as petroleum-derived fuels, due to the lack of oxygen content and similar hydrogen-to-carbon ratios (Probstein and Hicks 2006). The cetane numbers are quite high, so that the straight-chain fuel must be blended with lower-quality fuels for use in diesel engines (Dry 2002a) or be branched via oligomerization reactions to a cetane number around 50 for use as a pure diesel fuel (Dry 2002b). Blending FT synthetic diesel with FAME biodiesel or petroleum diesel is used to improve also the lubricity of the fuel (Gill et al. 2011); otherwise to be used pure, the FT diesel needs to be mixed with specialized aromatic additives (Corporan et al. 2011). The high cetane number of FT or hydrotreated-renewable-diesel fuels and their lack of aromatic content are considered to be the primary factors responsible for the observed decrease in NO_x, soot, unburned hydrocarbon, and CO emissions and increase in thermal efficiency, compared to conventional diesel (Szybist et al. 2005; Knothe 2010; Gill et al. 2011).

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