



A Broad Introduction to First-, Second-, and Third-Generation Biofuels

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Abstract

The aggregating usage of fossil fuels, rising demand for energy, fluctuating fuel prices, and increasing emissions of greenhouse gases are some of the concerning factors contributing to a shift in the interest from fossil fuels to biofuels. Biofuels are carbon-neutral sources of energy as the CO₂ emissions resulting from their combustion is utilized by the plants during photosynthesis leading to no net increase in atmospheric CO₂ levels. It is indispensable to focus on the new approaches to the research, development, and production of biofuels and their processing technologies to reshape a sustainable bioeconomy. Biofuels can be categorized into first, second, and third generation depending on the feedstock used for their production. The product range for first-generation biofuels is largely limited to ethanol produced from corn and distillers grains. In contrast, the second-generation biofuels are produced from non-food residues or lignocellulosic biomass such as agricultural biomass and forestry refuse, as well as energy crops. The third-generation biofuels are produced from algae, sewage sludge, and municipal solid wastes. This chapter comprehensively focuses on various first-, second-, and third-generation biofuels with emphasis on their biomass sources,

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fuel properties, and applications. The fuel products broadly discussed in this chapter are ethanol, butanol, bio-oil, biodiesel, algal oil, hydrogen, biomethane, and aviation fuel.

Keywords

Biofuel · Biomass · Bioethanol · Biobutanol · Bio-oil · Biodiesel · Algal oil · Hydrogen · Biomethane · Aviation fuel

1.1 Introduction

Today, almost every field is being explored for a better energy usability and productivity. The worldwide economy is drastically driven by fossil fuels, especially gasoline, natural gas, and coal. These fossil energy sources are the primary fuels to generate electricity and power for domestic and industrial purposes. Rapid industrialization at a global scale is the leading cause of the momentous consumption of fossil fuels. However, a sustainable economic and industrial development necessitates the utilization of a safer form of energy that would not generate any environmental pollutants or emissions.

The global energy consumption in 2008 was 533 EJ. However, with the increasing demand, the projection likely to increase to 653 EJ in 2020 and 812 EJ in 2030 (USEIA 2011). Figure 1.1 illustrates the worldwide production of petroleum and other liquid fuels. The top ten countries with the highest production of petroleum and other liquid fuels include the United States, Saudi Arabia, Russia, China, Canada, Iraq, the United Arab Emirates, and Brazil (USEIA 2017). The exploiting

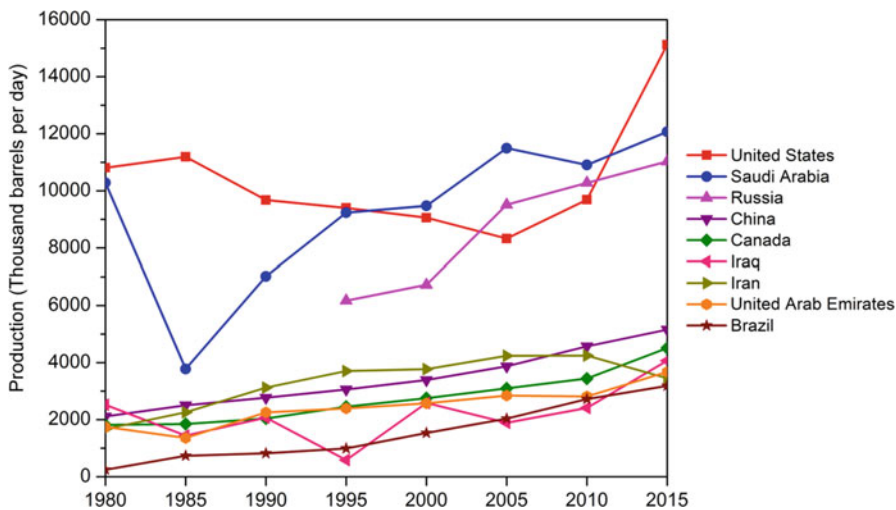


Fig. 1.1 Worldwide production of petroleum and other liquid fuels. (Data source: USEIA 2017)

consumption of fossil fuels is leading to an unparalleled increase in the greenhouse gas emissions and consequently global warming. The total CO₂ emission by the burning of fossil fuels in 2008 was 32,083 million metric tons (MMT) which increased from 5977 MMT in 1950 and 1958 MMT in 1990 (Boden et al. 2009). The worldwide energy-related CO₂ emissions are illustrated in Fig. 1.2. The non-OECD countries demonstrated a relatively higher CO₂ emissions compared to that of OECD countries. Particularly in 2015, the energy-related CO₂ emissions by the non-OECD and OECD countries were 18,517 MMT and 12,942 MMT, respectively. At a global scale, the CO₂ emissions rose from 21,536 MMT in 1990 to 31,459 MMT in 2015. However, the CO₂ emission is projected for increasing to 36,376 MMT in 2025 and 42,386 MMT in 2035.

The use of biofuels produced from renewable and biogenic materials has the tendency to mitigate greenhouse gas emissions, supplement the growing energy needs, improve the overall energy efficiency of existing fuel systems, and invigorate employment in bio-based sectors (Nanda et al. 2015). The large focus on biofuel production could replace the use of gasoline and other fossil fuels in the near future. Several developed and developing nations are emphasizing on developing their bioenergy market and established intergovernmental strategies for the use of biofuels.

Biofuels can be produced from a variety of feedstocks including agricultural crop residues, forestry biomass, energy crops, livestock manure, municipal solid waste, sewage sludge, industrial effluents, and other organic waste streams. These waste materials are rich in organic matter that could be recovered for conversion to biofuels through a variety of thermochemical and biochemical technologies. The purpose of

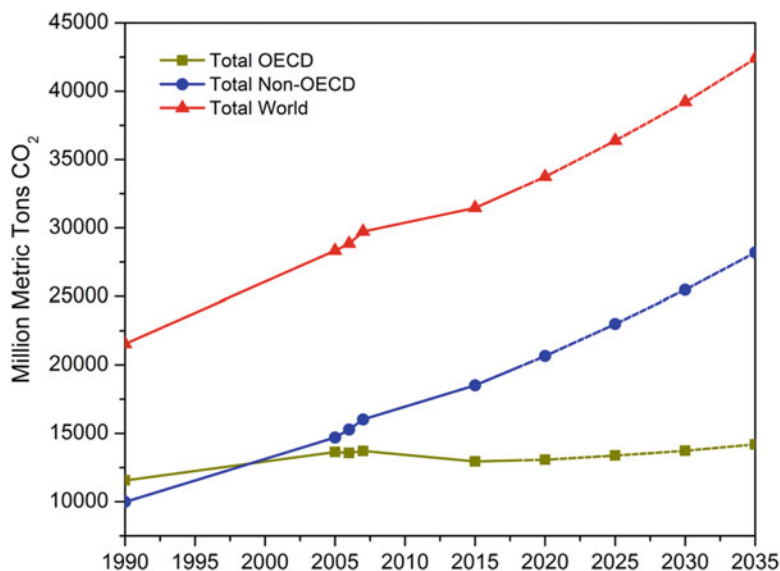


Fig. 1.2 Worldwide energy-related emission of CO₂. (Data source: IEO 2010)

this chapter is to give an introductory overview of different biomass sources and the classification of biofuels produced from them. This chapter aims to discuss different first-, second-, and third-generation biofuels along with their composition and properties. With this knowledge on the perspective of different classes of biofuels, the discussion is made on production and environmentally benign application of each of the fuels such as ethanol, butanol, bio-oil, biodiesel, algal oil, hydrogen, biomethane, and aviation fuel.

1.2 First-, Second-, and Third-Generation Biomass Sources

In a biorefinery perspective, biomass refers to a generic term for all organic material that could be potentially converted to fuels and chemicals. Biomass is a renewable and non-fossil composite biogenic organic material formed by natural or anthropogenic processes. It is obtained as a result of photosynthesis in plants, algae, and some bacteria via the conversion of solar energy to carbohydrates and lipids. In chlorophyll-containing living organisms, CO₂ reacts with water in the presence of sunlight to produce carbohydrates as the building blocks of biomass. Biomass broadly includes agricultural residues, forest residues, wood processing wastes, dedicated energy crops, animal manure, poultry litter, municipal solid wastes, industrial effluents, sewage sludge, and any other biogenic waste. It is indispensable to categorize the diversity of biomass sources to better understand the type of biofuels they produce. Figure 1.3 shows a schematic of different feedstocks and the resultant biofuels.

The first-generation biomass mostly includes food crops; hence, they appear unjustifiable for commercial use because of the food-versus-fuel controversies. The first-generation biomass includes edible plant materials and crops such as corn, wheat, sugarcane, and food grains (distillers grains). The second-generation biomass includes nonedible plant residues such as straw, wood, grasses, etc. Unlike first-generation biomass (starch-based feedstocks) that can be directly used in biorefineries for fuel production, the second-generation biomass requires a series of pretreatment to recover the fermentable sugars. Therefore, the utilization of second-generation biomass requires additional processing steps and operational cost for biofuel production.

Tremendous amounts of agricultural crop residues are obtained throughout the world as a result of agricultural and farming practices. Some commonly available agricultural biomasses include wheat straw, barley straw, flax straw, paddy straw, corncob, corn stover, cotton stalk, mustard stalk, canola meal, canola hull, flax fiber, jute bast, coconut coir, coconut shell, palm seeds, rice husk, walnut shell, almond shell, cashew nut shell, hazelnut shell, peanut shell, peach pits, plum pits, olive pits, apricot pits, sugarcane bagasse, etc.

The forest residues from softwood and hardwood species include stems, barks, twigs, cones, and needles. On the other hand, wood processing facilities generate biomass in the form of sawdust, wood chips, lumps, bales, pellets, and briquettes.

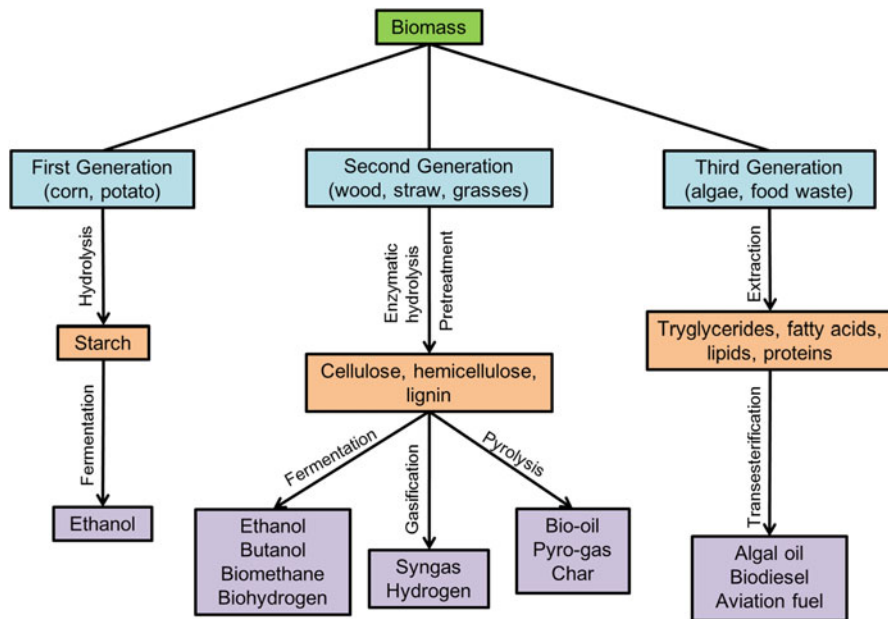


Fig. 1.3 A schematic overview of the basic steps in the production of first-, second-, and third-generation biofuels

Wood processing facilities generate fuel wood, char, and black liquor, which are chief sources of electricity in the United States, Brazil, Canada, Finland, and Sweden (FAO 2008).

Energy crops are considered as a second-generation feedstock due to their lignocellulosic composition and as third-generation feedstock owing to their fast-growing properties and less maintenance/nutrient requirement. Energy crops or dedicated energy crops are specifically cultivated for the purpose of converting them into fuel and energy. The energy crops can be both herbaceous (temperate grasses) and woody in nature. A few examples of energy crops are switchgrass, timothy grass, elephant grass, reed canary grass, ryegrass, *Miscanthus*, alfalfa, bamboo, hybrid poplar, and short rotation coppice. Perennial grasses are ideal energy crops because of high yield of biomass, round-the-year availability, fast growth, less farming needs, low nutrient requirements, low cost of production, tendency to regenerate in less fertile soil, and resistance to extreme weather conditions.

The third-generation biomass includes microalgae and macroalgae. Marine biomasses such as seaweed, hyacinth, caltrop diatoms, duckweed, kelp, and salvinia have candidacy for the production of biofuels, especially biodiesel (Vassilev et al. 2012). Aquatic biomass is considered third-generation biomass and advanced biofuel feedstock due to their perennial and inherent growth, high growth rate, as

well as no competency with arable land and crops for space, sunlight, and nutrients. While soybean and canola produce 200–450 l of biodiesel, algae are capable of producing 61,000 l/ha of biodiesel (Savage 2011). Algae can produce different types of biofuels including bioethanol, biodiesel, syngas, and biohydrogen (Demirbas 2010). Another category of biomass includes animal manure (e.g., poultry litter, dairy manure, and swine manure), municipal solid waste, industrial effluent (textile effluents, paper and pulp industry wastes, tannery effluents, pharmaceutical wastes, etc.), and sewage sludge.

Among all the categories of biomass, the major interest of biorefineries is on second-generation and third-generation biomass. The second-generation biomasses are mostly lignocellulosic materials comprised of cellulose, hemicellulose, and lignin. These components have the candidacy for being transformed into energy-dense hydrocarbons and fine chemicals. The conversion routes involve thermochemical and biochemical pathways and technologies such as biomass-to-liquid (e.g., pyrolysis, liquefaction, and fermentation), biomass-to-gas (gasification and methanation), and gas-to-liquid (Fischer-Tropsch synthesis and syngas fermentation) (Nanda et al. 2014b).

Lignocellulosic biomass typically consists of 30–60% cellulose, 20–40% hemicellulose, and 15–25% lignin (Nanda et al. 2013). Cellulose is a linear and crystalline homopolymer of repeating D-glucose subunits linked by β -1,4 glycosidic bonds. Hemicellulose is an amorphous short-chain heteropolymer containing pentose sugar (β -D-xylose, α -L-arabinose), hexose sugar (β -D-mannose, β -D-glucose, α -D-galactose), and sugar acids (α -D-glucuronic, α -D-4-O-methylgalacturonic, and α -D-galacturonic acids). Lignin is an amorphous, hydrophobic, and aromatic polymer of *p*-hydroxyphenylpropanoid units linked via C–C and C–O–C bonds. It is a result of oxidative polymerization of three monolignols, namely, *p*-coumaryl, coniferyl, and sinapyl alcohols. Lignin, present in plant cell wall, covalently binds with cellulose and hemicellulose, thus giving mechanical strength to the plant and recalcitrance to microbial and insect attack.

Corn ethanol, one of the first-generation biofuels, is profitably and commercially produced from food crops such as corn, wheat, and sugarcane. However, first-generation biofuels have many drawbacks such as: (1) social unacceptance and ethical concerns due to diversion of food crops as feedstocks, (2) lack of diversity in feedstock selection, and (3) competition for arable lands for cultivation of biofuel crops rather than harvesting food crops (Nanda et al. 2015). In contrast, second-generation biofuels such as bioethanol (cellulosic ethanol) and biobutanol do not pose any threat to the food supply or competition to arable lands. This is because second-generation biofuels are derived from nonedible plant biomass, especially lignocellulosic feedstocks. The use of second-generation biofuels can reduce the demand for first-generation biofuels and avoid the direct competition with agricultural crop harvests. Additionally, second-generation biofuels have considerably lower greenhouse gas emissions during their life cycle (Wang et al. 2007). Table 1.1 summarizes the properties and benefits of some first-, second-, and third-generation biofuels, namely, bioethanol, biobutanol, bio-oil, algal oil, biodiesel, biohydrogen, biomethane, and aviation fuel.

Table 1.1 Typical properties of some first-, second-, and third-generation biofuels

Biofuel	Feedstock	Fuel properties and advantages
Ethanol	Corn, distillers grains, molasses, straw, bagasse, woody biomass, and other lignocellulosic biomasses	Oxygenated fuel
		Blended with gasoline at flexible ratios
		High fuel concentrations require vehicle engine modification
Butanol	Corn cobs, straw, woody biomass, grasses, and other lignocellulosic biomass	Superior fuel properties than ethanol and comparable with gasoline
		No blends with gasoline required
		Compatible with the current vehicle engines at high concentrations
Bio-oil	Lignocellulosic biomass, waste organic materials, and waste rubber	Energy-dense fuel source
		Can be used directly to generate power in-house refinery
		Precursor of fine chemicals and industrially relevant bio-products
Algal oil	Microalgae and macroalgae	Cultivation of algae can lead to CO ₂ capture in parallel with oil production
		Algal oil is rich with triglycerides and fatty acids
		De-oiled algae can be used a nutrient-rich diet for livestock
Biodiesel	Vegetable oil, algal oil, and animal fats	Improves lubricity compared to that of conventional diesel
		Produced through transesterification of nonedible oil and waste edible oil
		High energy density compared to alcohol-based fuels
Hydrogen	Lignocellulose biomass, algae, water, sewage sludge, and industrial effluents	Superior heating value of 140 MJ/kg
		Energy carrier and vector
		Feedstock for fuel cells
		It's a clean fuel as its burning produces only water and no emission of pollutant and particulates
Biomethane	Waste organic materials and lignocellulosic materials	Production of biomethane requires less maintenance and capital investment
		Invigorates rural livelihood and employment
		Independent on seasonal and geographical variations
		Biomethane can be used as a domestic cooking fuel and in household heating and electricity generation
Aviation fuel	Halophytes, lignocellulosic biomass, sewage sludge, algae, <i>Camelina</i> , <i>Jatropha</i> , and oilseed crops	Its utilization decreases the dependence on fossil resources
		Reduces environmental impacts from aviation-related emissions
		Uses cheaply available feedstocks
		Blends of biokerosene and conventional aviation fuels can reduce the fuel cost

1.3 Bioethanol

Some low molecular weight alcohols that have pronounced potential to replace fossil fuels include methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), and butanol ($\text{C}_4\text{H}_9\text{OH}$). Recently, ethanol has emerged as a biofuel with a great deal of interest in its production and utilization. Among the several alternative renewable fuel sources, bioethanol has proven efficient by a mass-scale production and usage. Bioethanol is produced through fermentation of starchy materials (first-generation biomass) and lignocellulosic substrates (second-generation biomass) using the widely known *Saccharomyces cerevisiae*. Bioethanol barely covers the fuel industry as it is majorly dedicated toward the alcohol and beverage industry. Ethanol that is produced for nonconsumable applications is made unfit for human intake by adding small amounts of toxic and unpleasant substances such as traces of methanol or gasoline (Gnansounou and Dauriat 2005; Balat and Balat 2009a, b). Ethanol is an oxygenated fuel containing 35% oxygen, which exhibits clean burning characteristics such as reduction in greenhouse gas emissions and particulate matters along with the benefits of low vapor pressure (Nanda et al. 2014b).

The application of ethanol as an alternative fuel source has a significant historical background. The first internal combustion engines capable of using ethanol as the fuel were designed by Samuel Morey in 1826, and the following notable ones were designed in 1876 by Nicholas Otto (Demirbas and Balat 2006). The first successful car that could run on pure ethanol was produced by Henry Ford in 1896. This led to the manufacturing of the Ford Model T car series in 1908 that were flexible in using ethanol or a gasoline-ethanol blend as the fuel (Solomon et al. 2007). Europe and the United States had a widespread use of ethanol as fuel until the 1900s. However, after the First World War, the demand for ethanol diminished as its production became more expensive than the processing of petroleum-based fuels. Nonetheless, there was still an interest subsisting in industries like General Motors and DuPont to use ethanol as an anti-knock agent and as a possible replacement of the conventional fossil fuels (Mussatto et al. 2010).

Ethanol has already captured a large-scale production market in the countries like Brazil and the United States and some European nation. It is expected to become a dominating biofuel for the transport industry within the next 20 years. Ethanol can either be blended with gasoline or used in its pure form for some newly developed advanced flex-fuel hybrid vehicles (Gnansounou and Dauriat 2005; von Blottnitz and Ann 2007). Ethanol has several advantages over the conventional fuels owing to its higher octane number, high heat of vaporization, and sustainability. The use of bioethanol as an octane enhancer in unleaded gasoline could replace methyl tert-butyl ether (MTBE). Ethanol could also be used as an oxygenated compound for the clean combustion of gasoline for an improved air quality (Gnansounou and Dauriat 2005). The other benefits of bioethanol are its lower emissions of greenhouse gases. Ethanol has an ability to replace 32% of gasoline usage when used as an E85 blend (i.e., 85% ethanol and 15% gasoline).

Brazil and the United States supply 90% of the world's total ethanol production (Nanda et al. 2014b). Currently, sugarcane (in Brazil) and corn (in the United States)

are widely being used for ethanol production with major application in the fuel industry at competitive prices. It is necessary to understand here that these raw materials for ethanol production cannot be sustained in the long term as they are first-generation biomass (food materials). Furthermore, another challenge is that the emission of greenhouse gases resulting from the consumption of ethanol obtained from sugar or starch as fuel is not as low as desired. Thus, there is an immediate need for exploring lignocellulosic feedstocks in the form of agricultural residues and forest residues for the production of ethanol.

The substrates for bioethanol production include directly fermentable sugars (pentose and hexose), starch-based materials, and lignocellulosic feedstocks. The established process for ethanol production from sugarcane and starch-based feedstocks involves the conversion of starch to ethanol through liquefaction step (to enhance the solubility of starch), followed by the hydrolysis step that results in the production of glucose. The next step involves the fermentation of glucose to ethanol using solventogenic fungi and bacteria. The bioconversion of lignocellulosic biomass involves biomass pretreatment (acid, alkali, ionic, or mechanical), delignification, enzymatic hydrolysis, and fermentation (Nanda et al. 2014a). The pathway for ethanol production from lignocellulosic biomass is not entirely similar to starch-based process because of the requirement of biomass pretreatment. Additionally, the technical and economic challenges in producing ethanol from lignocelluloses are yet to be addressed (Gnansounou and Dauriat 2005; Demirbas and Balat 2006; Mussatto et al. 2010).

Hahn-Hägerdal et al. (2006) have reviewed the current developments in the bioconversion processes that targeted ethanol production as a fuel with emphasis on the improvement and development of process integration. The cost of feedstock for ethanol production varies considerably from US \$22 to 61 per metric ton of dry matter. This makes the total cost rely on the plant capacity, making it a major contributor to the total production cost. The cost of hydrolysis specifically for the enzymatic process contributes majorly to the production cost (Hahn-Hägerdal et al. 2006).

Certain drawbacks of ethanol prevent its widespread use at the commercial level. Firstly, it takes more volume (1.5 times) of ethanol to produce the same energy as gasoline. Secondly, ethanol is corrosive to the rubbers used in the gaskets and fuel lines of older vehicles. However, this problem has been addressed in the newer vehicles that run entirely on ethanol. Lastly, ethanol tends to absorb water from the atmosphere, which dilutes it and makes its transportation through pipelines a challenging task. Biobutanol emerges as a suitable alternative to ethanol in addressing these challenges.

1.4 Biobutanol

Biobutanol is another alcohol fuel that enlists itself in the list of potential second-generation biofuels. It was traditionally used as a solvent in various products such as cosmetics, detergents, hydraulic fluids, antibiotics, and drugs, as well as an

intermediate in the manufacturing of methacrylate and butyl acrylate. It is also used as an extractant in the synthesis of many pharmaceutical products. However, the exploitation of butanol as a biofuel is a relatively new application in the fuel market. Butanol, when compared to ethanol, is less volatile and explosive. In addition, butanol has a lower vapor pressure (0.3 psi) and higher flash point (35 °C), which makes it safer to handle. The heating value of butanol (29.2 MJ/L) is higher than that of ethanol (21.2 MJ/L). Moreover, the air-to-fuel ratio (11.2) and octane ratings (96) of butanol are almost comparable to gasoline, which gives it an edge over other alcohol-based fuels. It is less hygroscopic unlike ethanol (that absorbs water from the atmosphere) and is miscible with gasoline in any proportion (Nanda et al. 2017). Butanol can be directly used as a drop-in fuel or as blends with gasoline or diesel and can be easily supplied using the existing pipelines (García et al. 2011).

Louis Pasteur in 1861 was the first to report the production of butanol using microbial fermentation. Later, Albert Fitz progressively worked on extracting butanol from glycerol using two strains of bacteria. Additionally, researchers like Beijerinck, Bredemann Sharding, and Pringsheim made significant contributions to this field. Biobutanol was industrially synthesized in a large scale during 1912–1914 by the well-known acetone-butanol-ethanol (ABE) fermentation from molasses and cereals with the help of strains like *Clostridium acetobutylicum* (Dürre 2008). It is during the First and Second World War that sugar and cereals were the main substrates for ABE fermentation. Due to the increased food demand during the war, these feedstocks became too expensive and scarce in supply, which led to a shrinking interest in ABE fermentation. Thus, there is a lot of scope for exploring different low-cost raw materials for fermentative butanol production that can lead to its cost-effective biosynthesis. Abundantly available and inexpensive lignocellulosic biomass such as agricultural waste (barley straw, corn stover, corn fiber, wheat straw, switch grass, timothy grass) and wood residues can be used for an efficient and economical ABE fermentation (Nanda et al. 2014a). Until recently, the use of butanol was primarily limited to industrial solvent or precursor for fine chemical production. Recently, DuPont and British Petroleum have announced a joint initiative to commercialize the production of biobutanol through ABE fermentation (Kumar and Gayen 2011).

Butanol production can be through either petrochemical pathways or fermentative pathway. The commonly used chemical synthesis route for butanol production is the oxo process. This process involves the catalytic reaction of propylene with carbon monoxide and hydrogen. The intermediate products formed are *n*-butyraldehyde and isobutyraldehyde, which are hydrogenated to produce *n*-butanol and iso-butanol, respectively (García et al. 2011). The biological pathway involves batch, fed-batch, and continuous production of butanol through ABE fermentation. ABE fermentation is carried out by *Clostridium* species, mostly *Clostridium acetobutylicum* and *Clostridium beijerinckii* in two phases. In the first phase of fermentation, monomeric sugars are converted to acetate and butyrate, which in the next phase are converted to acetone and butanol, respectively (Qureshi and Ezeji 2008). The typical products of ABE fermentation are acetone, butanol, and ethanol in the mass ratio of 3:6:1. Various feedstocks and microbial strains are used to obtain

better butanol yields at lower production costs. Different metabolic engineering and genetic engineering approaches have been applied to butanol-producing *Clostridium* to enhance butanol production and suppress the product inhibition (Nanda et al. 2017). Kumar and Gayen (2011) have discussed the available strains for the production of biobutanol and the different fermentative pathways involved in detail along with some recent developments in the field of biobutanol production.

Green (2011) has elaborately discussed the industrial perspective for the fermentative production route of biobutanol. It is reported that China stands top in the list of leading countries that invest in the re-commercialization of ABE fermentation. It is believed that more than US \$200 million has been invested by China to increase its annual butanol production from 0.21 to 1.0 million tons. Only a few plants in China majorly produce butanol (30,000 tons per annum) by using cornstarch as the feedstock in semicontinuous fermentation (Green 2011). China is foreseeing to retrofit its existing conventional starch-based refineries to use cheaper cellulosic materials as feedstock for butanol production. This approach of retrofitting old refineries as well as pulp and paper industries seems to be an attractive alternative to accelerate the production of biobutanol in developed countries like Brazil and the United States.

Several studies prove that blending butanol with diesel and other fuels can also be a promising attribute. Yilmaz et al. (2014) studied the effect of different blends of butanol-biodiesel on the performance and emission on the indirect injection engine. It was found that in comparison with biodiesel, the blended fuel showed lower rates of emission of nitrogen oxides with higher greenhouse gases and hydrocarbons emissions. Giakoumis et al. (2013) reviewed the exhaust emissions of *n*-butanol blends with diesel on engines working under transient conditions. The essential mechanisms of exhaust emissions during transient operation of the engine were discussed on the basis of fundamentals such as transient operation and properties of butanol in comparison with diesel.

Jin et al. (2011) reviewed the properties of butanol that make it a better biofuel than ethanol and biodiesel along with the developmental strategies in butanol production. Several methods that involved advanced fermentative techniques and metabolic engineering application on the strains were discussed. It was reported that butanol is a potential fuel as compared with gasoline or diesel fuel on the basis of its combustive properties, engine performance, and emissions from the exhaust (Jin et al. 2011). Butanol as a fuel has several advantages; however, it is important to understand the drawbacks associated with it. Butanol contributes to the formation of photochemical smog on its reaction with volatile organics present in the atmosphere. Butanol causes irritation to the human eyes, throat, and nose, and it is highly flammable. Most importantly, *Clostridium* suffers from inhibition of butanol as 2% butanol in the fermentation medium initiates microbial inhibition. Owing to the low butanol yields, its separation becomes a tedious and expensive process, unlike ethanol. These limitations though significant cannot overshadow the benefits of using butanol as a second-generation biofuel; hence there is a huge scope for research in its prospective production and utilization as an advanced biofuel.

1.5 Bio-oil

Biomass has been identified as a prominent renewable energy source to compensate the depleting fossil fuels. The major constituents of biomass are carbohydrates, which are rich in carbon, hydrogen, and oxygen with possibly high energy content. Bio-oil also termed as pyrolysis oil is mostly produced through biomass pyrolysis. It contains numerous aromatic compounds such as alkanes, phenol derivatives, and aromatic hydrocarbons and trace amounts of esters, ketones, ethers, amines, sugars, and alcohols with a H/C molar ratio usually higher than 1.5. It is produced in the oxygen- or air-deprived environment during biomass pyrolysis at high temperatures. Bio-oil is portable to be used as direct fuel in boilers, or it can be further upgraded to produce fuel or other industrial chemicals by using advanced methods such as catalytic or zeolite cracking, hydrogenation, and processing the aqueous phase (Isahak et al. 2012).

The two major techniques used for biomass conversion to bio-oil can be broadly categorized as the fast pyrolysis and hydrothermal liquefaction. Pyrolysis is the rapid decomposition of organic compounds at high temperatures in an inert atmosphere to produce bio-oil, pyro-gas, and char. Hydrothermal liquefaction, on the other hand, involves the treatment of biomass at high temperatures and pressure in the presence of water and a suitable catalyst. The effects of fast and slow pyrolysis of lignocellulosic biomass on the production of bio-oil, char, and gases have been discussed by several authors (Nanda et al. 2014c; Mohanty et al. 2013; Mohan et al. 2006). Fast pyrolysis featured by its high heating rates and short vapor residence time results in greater yields of bio-oil, whereas slow pyrolysis characterized by its slow heating rate and longer residence time leads to higher yields of char.

Moisture-free biomass is preferred in the case of pyrolysis, but for hydrothermal liquefaction, a relatively moist biomass is suitable. The presence of moisture in biomass renders hydroxyl and carboxyl groups to the bio-oil derived through pyrolysis, which reduces its heating value and compromises the fuel properties. Although there have been significant contributions to explore the technique of fast pyrolysis for the production of bio-oil, the hydrothermal liquefaction technology remains in its natal state (Xiu and Shahbazi 2012).

Along with the existing techniques of fast pyrolysis and hydrothermal liquefaction, hydrotreating is a budding process that can potentially convert the biomass into petroleum-compatible products. Out of the various reactions taking place during hydrotreating is hydrodeoxygenation to remove oxygen-containing functional groups (carboxyl and hydroxyl) from the bio-oil. The steps involved in bio-oil upgrading through hydrotreating route include purification of the bio-oil, modification of the bio-oil through chemical processing, removal of heteroatoms, breaking of the long hydrocarbon chains, and separation. However, it is critically significant to recognize these elements as multiple unit procedures or as a single unit in order to obtain a fuel product that can be either a part of the bio-oil production route or as a part of petroleum processing or conversion (Zacher et al. 2014).

The catalytic upgrading route for bio-oil purification is established over the same application of hydrotreating. However, in its crude form, bio-oil has a high content

of oxygen, which gives it low stability and poor heating value. The widely used hydrotreating catalyst Co-MoS₂/Al₂O₃ or other metal catalysts can be used for this purpose. The major challenge in this process is catalyst fouling due to high carbon deposition that gives the catalyst a lifetime as short as 200 h. Zeolites have been found to be a promising alternative. Zeolite cracking can be used for deoxygenation with the catalyst like HZSM-5. As deoxygenation reaction does not require hydrogen, the processing can be completed under atmospheric pressures. Furthermore, the bio-oil produced is low in hydrogen content, which leads to a low H/C ratio. Thus, it can be inferred that bio-oil produced over zeolites is of poor grade, with heating values that are almost 25% lower than the crude oil. Zhang et al. (2006) studied the upgrading of bio-oil using different solid catalysts. The study involved a comparative analysis of the effects of using solid acid catalyst 40SiO₂/TiO₂-SO₄²⁻ and solid base catalyst 30K₂CO₃/Al₂O₃-NaOH on the upgrading of bio-oil, and the properties of the product from both the processes were analyzed and discussed in detail.

There are several other studies that discuss the progress in the field of bio-oil production, upgrading, and commercialization from various sources (Jacobson et al. 2013). Hydrodeoxygenation seems to be the best route for bio-oil upgrading as deoxygenation through zeolites does not produce bio-oil of acceptable grades to compete with crude oil. A few technical advances can be contributed through catalyst synthesis for demonstrating better activities, enhanced kinetics, mechanism of carbon formation, prediction of appropriate hydrogen pressure, and understanding the deactivation caused by sulfur (Mortensen et al. 2011). Though the use of bio-oil is promising, there is a long way to trace toward its complete commercialization as a finished product that can compete with the crude oil.

1.6 Algal Oil

The past few years have gained further advancement in the field of biofuels with different alternatives being tried as the feedstock for biofuel generation. In this respect, algae have been an option of immense interest. The benefit of using algae as a source of biofuel is that higher productivities as compared to terrestrial plants. Some algal species are capable of accumulating large amounts of triacylglycerides, which form the major precursor for biodiesel production. Moreover, owing to its aquatic nature, there is no requirement for highly fertile agricultural land to cultivate algae as a third-generation biofuel feedstock. Algae produce more oil than most other agricultural biomass used. It is reported that algae are capable of producing 250 times more oil as soybean grown per acre (Hossain et al. 2008). A few of the algal strains used for the production of algal oil are cyanobacteria (*Chloroxybacteria*) and eukaryotic microalgae, e.g., green algae (*Chlorophyta*), red algae (*Rhodophyta*), and diatoms (*Bacillariophyta*) (Brennan and Owende 2010).

In biological terms, algae are one of the oldest plants that belong to the family of thallophytes that lack roots, stems, and leaves and have an uncovered reproductive cell. The major photosynthetic pigment present in algae is chlorophyll. The simple cell structure of algae makes them efficient solar energy harvesters and adaptable to

prevailing environmental situations in the long run (Brennan and Owende 2010). Several biofuels that can be derived from algae include methanol (produced from anaerobic digestion of algae), biodiesel (produced by processing of algal oil), and biohydrogen (photobiologically produced by algae).

Unicellular green algae majorly contribute to the production of biodiesel. It is a photosynthetic eukaryote with high population density and high growth rates. In favorable conditions, it can replicate its biomass to double in less than a day. In addition, it is capable of having high cell density with high lipid content. The biodiesel produced from algae has energy density similar to conventional diesel fuel. The heating value for algal oil (biodiesel) is dependent on the biomass source and comparable to the high values of the conventional diesel. The heating value for algal oil (41 MJ/kg) is more than that of oils produced from other biomass such as for rapeseed (39.5 MJ/kg). This further improves the heating values for the biodiesel derived from algal oil as compared to the biodiesel from other biomass. Although the agricultural biomass is a common feedstock for the production of biodiesel, algal oil stands strong in competing to make its place in the list at a commercial level (Demirbas 2011).

The most common methods to extract oil from algae are the expeller or pressing method, an extraction process with hexane as a solvent and supercritical fluid extraction. Biodiesel from algae contains mono-saturated and saturated fatty acids. Typically, an algal oil contains 36% oleic acid, 15% palmitic acid, 11% stearic acid, 8.4% iso-linoleic, and 7.4% linoleic acid (Demirbas and Demirbas 2011). The benefit of algal oil is that the fuel polymerization during combustion is less due to mono-saturated and saturated fatty acids as compared to fuels with polyunsaturated acids. When the algal oil is extracted, refused biomass can be used as a protein-rich feed for livestock. This adds to the relevance of this process with less strain on waste handling. The process of biodiesel production from algae is similar to the biodiesel production from vegetable oil. However, the benefits of less competition for arable land as compared to agricultural biomass and more efficiency of the products are magnificent (Demirbas and Demirbas 2011; Greenwell et al. 2010; Scott et al. 2010).

Some of the challenges of algal oil cannot be overlooked. The commercial and sustainable production of algal oil at optimized conditions is yet to be established. In particular, the optimization of algal biomass production and the triacylglyceride content need more research attention. The limitation of light penetration in the cultured algae can be a concern for low biomass production. The high water content of the algae biomass needs more energy for its drying, which makes the process expensive. The overall capital cost of the production of algal biomass is higher than the production of agricultural biomass, especially for the regions with less sunlight. All these challenges question the use of algae for biodiesel production, but the benefits of the process are much more. This calls for further intensive research in this field for an optimum and efficient utilization of algae as a third-generation biomass for biodiesel production.

1.7 Biodiesel

Rudolf Diesel became the first person to use vegetable oil for his diesel fuel engine (Shay 1993). During 1930–1940, initial use of biodiesel (vegetable oils) as fuel for diesel engines was witnessed. Biodiesel is an unconventional fuel source for the internal combustion engines and can be chemically categorized as a combination of monoalkyl esters with long-chain fatty acids extracted from biomass. The typical alkyl fatty acid chain in biodiesel ranges from C_{14} to C_{22} esters of ethanol or methanol. This chemical nature makes biodiesel a suitable substitute for the conventional diesel fuel.

There are various sources of vegetable oils that contain glycerides as a potential fuel source replacing the conventional diesel fuel. The high heating power and sulfur-free exhaust gases from vegetable oil-derived fuel combustion make it suitable for biodiesel production. Since plants are the essential source of vegetable oils, their consumption as the fuel produces CO_2 that is biologically recyclable. It is only due to the high viscosity of the biodiesel from vegetable oils that a modification in the commercial diesel engine is required, as the rest of the properties remain compatible. The kinematic viscosity of vegetable oil ranges from 30 to 40 cSt at 38 °C. This viscosity is almost 20 times higher than the viscosity of diesel fuel. The cetane number for vegetable oil varies from 32 to 40, which makes it a better fuel. Another option to enhance the performance of biodiesel as a direct engine fuel is to blend it with the conventional diesel as they are both miscible.

The reaction for biodiesel production occurs in the presence of a suitable catalyst (usually a strong base, e.g., NaOH or KOH) that leads to the production of methyl esters. These methyl esters are termed as biodiesel. The major challenges for swapping diesel fuel with biodiesel are due to the high viscosity, polyunsaturated nature, and low volatility of the biodiesel. Thus, the vegetable oils undergo processing to produce a suitable biodiesel that has comparable properties to that of the commercial diesel. The three main processes observed to achieve the target properties of biodiesel are pyrolysis, transesterification, and microemulsions. Dedicated research has been conducted on the use of biodiesel as diesel engine fuel. The divergent feedstock materials have been tested for the production of biodiesel, which includes palm oil, sunflower oil, soybean oil, rapeseed oil, coconut oil, and tung oil. Animal fat has also been explored as an alternative source of biodiesel, but it lacks detailed study as the vegetable oil.

Fukuda et al. (2001) reported that enzymatic transesterification has a great contribution toward biodiesel production. The technologies related to biodiesel upgrading were reviewed focusing on transesterification using a catalyst (acid or alkali), supercritical fluid, and lipase enzyme with an industrial viewpoint. Marchetti et al. (2005) highlighted the alternative technologies that could be employed to produce biodiesel. Various studies with different oils, catalysts, and alcohols have been conducted to produce biodiesel. Transesterification is dominated by factors like reaction conditions, alcohol-to-oil molar ratio, water contents of oils or fats, purity of reactants, and amount/type of catalyst. Murugesan et al. (2009) attempted to compile the methods of biodiesel production, its quality analysis, its performance for internal

combustion engines, and its resource availability. Recommendations for developmental strategies for biodiesel, economic aspects, and environmental considerations are also detailed.

Although it is possible to use vegetable oil as fuel in the diesel engine in the form of biodiesel, there are certain challenges that cannot be overlooked. A few of these problems are the inefficient mixing of air with biodiesel that leads to high smoke emissions. The high flash point also attributes to lower volatility of biodiesel. High carbon deposition and failure of the injection nozzle in the diesel engine are other common drawbacks. These problems bring a scope for chemical modification of biodiesel to make it compatible and efficient for use in a diesel engine.

1.8 Hydrogen

Hydrogen is one of the most promising alternatives to the conventional fuels due to its most superior heating value of 141.8 MJ/kg. It is the secondary energy source that needs to be derived from renewable and nonrenewable hydrocarbon-based materials. Hydrogen is referred to as an energy carrier and vector. It is believed to have a great role as an energy carrier in the global energy sector of the future. Hydrogen is considered as a clean fuel as it emits only water and no CO₂ upon combustion. It is widely used in fuel cells for the generation of electricity.

Hydrogen has found application in combustion engines along with fuel cells in electric vehicles. Hydrogen is in its gaseous state at ambient temperatures and pressures, which exhibits a great challenge in its transportation and storage as compared to other liquid fuels. Since it is the second lightest element and highly flammable, it needs to have special and safe storage options. It can be stored physicochemically and chemically in different states or in the form of liquid compounds such as metal hydrides, alanates, methanol, or light hydrocarbons (Balat and Kirtay 2010).

Mostly, the engines are found to be specific to the fuel properties for efficient operation. However, hydrogen can be obtained from any of the conventional feedstock, and hence the engine can be easily modified for hydrogen use. This attribute makes hydrogen a universal fuel. Recently, many nations around the globe are focusing on the development of new technologies for hydrogen production with solutions to the energy security. Countries like the United States have initiated a multiyear plan with an entire focus on improving the infrastructure of hydrogen generation, its use as an energy source, and its storage techniques (Holladay et al. 2009).

The economy of hydrogen production depends on the availability of an economic and environment-friendly source. Current scenario witnesses hydrogen production from fossil fuels through steam and dry reforming of methane and natural gas. However, fossil fuels have a very limited supply and also emit harmful greenhouse gases during hydrogen production. Bartels et al. (2010) compared the production cost of hydrogen from fossils and alternative energy sources. The analysis of the study showed that the most economical route for hydrogen production was through

coal and natural gas, with an estimated cost of hydrogen to be 0.36–1.83 \$/kg and 2.48–3.17 \$/kg, respectively. Balat and Kirtay (2010) reported that hydrogen production from steam methane reforming costs in the range of 1.5–3.7 \$/kg (natural gas price around 7 \$/GJ), whereas hydrogen production from biomass costs around 10–14 \$/GJ. The increasing cost of fossil fuels might eventually lead to higher production costs of hydrogen; hence alternative energy sources might be a prospective source for hydrogen production.

Levin and Chahine (2010) reported the production of hydrogen from renewable feedstocks such as agricultural waste and other waste streams that contributed in minimizing the emission of greenhouse gases. This increases the flexibility and improves the economics of the production and distribution of hydrogen. Few of the processes that can be taken into account for hydrogen production from alternate energy routes are electrolysis, biological production, and thermocatalytic processes. These processes can be adapted to on-site hydrogen production avoiding the need to establish an expensive and large distribution infrastructure. Nonetheless, each of the alternate routes mentioned has its technical challenge in hydrogen production such as conversion efficiencies, purification of hydrogen, feedstock selection, and storage (Levin and Chahine 2010).

Hydrogen generation from biomass through gasification is certainly an essential route; however, this technology needs more development. Kirtay (2011) reviewed the recent advances in different hydrogen production technologies. It was reported that an efficient production of hydrogen requires a coproduct pathway to compete with hydrogen production from conventional crude processes such as steam reforming of natural gas. A potential route from biomass to hydrogen is through activated carbon, which involves a coproduct that is commercially practicable. Hydrogen production from biomass has several benefits with a major challenge that targets the economical production of hydrogen (Kirtay 2011).

It is known that the most cost-efficient method of hydrogen production that currently subsists is through steam reforming of methane and this process is commercially established. As discussed earlier, this process uses nonrenewable sources for hydrogen production and does not stand the test of sustainability. It is suggested that the cost of hydrogen production is predominantly dependent on the cost of feedstock. Thus, a cost-efficient energy generation process for hydrogen production from biomass should be established. Government policy interest in switching to hydrogen-based infrastructure is rising as hydrogen conversion to useable energy is more efficient than conventional fuels. Additionally, hydrogen produces only water as a by-product during its consumption as an energy source, unlike the fossil fuels that release greenhouse gases along with obnoxious nitrogen and sulfur compounds. To achieve a large-scale global production and utilization of hydrogen, strategic planning and cooperation among developed and developing nations are required (Balat and Balat 2009a, b).

1.9 Biomethane

Attempts to minimizing the dependency on land resources are progressively made for the sustainable production of second-generation biofuels. Biomethane is produced from the high moisture-containing biogenic wastes and biogas upgrading. It can also be produced from specific agricultural feedstocks such as grasses and maize, which have huge benefits but are overshadowed due to the limitations of the agricultural land use for other significant applications like food crop cultivation. To produce biomethane at a commercial scale, it is essential to develop and utilize the gasification techniques of woody biomass (Åhman 2010). A few of methanogenic bacteria are *Methanobacterium*, *Methanobacillus*, *Methanococcus*, and *Methanosarcina* (Molino et al. 2013).

Methane has high energy density (55.5 MJ/kg). Thus, it is of interest to the energy sector. The extraction of methane from biogas is usually employed through anaerobic digestion of the biomass. The primary product, i.e., the biogas, consists of CH₄ and CO₂, which is further purified to obtain clean methane. Apart from the main components, water vapor, siloxanes, ammonia, hydrogen sulfide, carbon monoxide, oxygen, and nitrogen are present in trace amounts in the biogas. For the purification of biogas to methane, there are two primary steps involved. The first step is to clean biogas for removing any trace impurities, and the second step involves upgrading to the clean biomethane for improving its physical properties like calorific value. Upgrading makes biomethane ready for use as a vehicular fuel meeting the stringent environmental standards.

There are several methods employed in obtaining clean methane, which depend on the properties of the feed gas such as fuel efficiency, operational properties, etc. A few of the methods employed are the condensation methods and drying methods. Different impurities are removed from biogas through specific techniques to obtain clean methane (Ryckebosch et al. 2011). The processing of the biogas also depends on the type of feedstock used. Nizami et al. (2009) discussed the various processes that could be used for biomethane production using grass as the feedstock.

There are several studies that deal with the production of biomethane using anaerobic digestion of the wet biomass from different sources such as land energy crops, ocean energy crops and organic wastes (Chynoweth 2005; Molino et al. 2013), grasses (Nizami et al. 2009), and starchy and lignocellulosic materials (Frigon and Guiot 2010). There have been several attempts to identify the best feedstocks for biomethane production from biogas. Patterson et al. (2013) compared the environmental constraints for the production and use of biomethane and its blends with biohydrogen from food waste and wheat feedstock on the basis of data from two separate laboratory runs. In the case of food waste, a two-step batch process gave higher hydrogen yields, but the overall energy efficiency was lower than the single-step process. Food wastes from landfill aided in reducing the burden on the environment as compared to diesel fuel, which posed several environmental damages. In the case of wheat feedstock, the overall energy outputs were high with low hydrogen yields in a two-stage semicontinuous stage. The significance of

outlining and optimizing biofuel production variables was highlighted (Patterson et al. 2013).

Countries like Italy and Ireland have made great efforts toward residue-based biofuel production. There are studies that evidently present the constant efforts of these nations toward waste usage from various industries for the production of biomethane (Patrizio et al. 2015; Thamsiriroj and Murphy 2011). The benefits of using biomethane as an alternative fuel source are many, and that forms the reason for the revival of this biofuel for the energy market utility. However, there are certain constraints of using biomethane which cannot be neglected. With the use of biomethane, there are high greenhouse gas emissions in the environment, and the properties of biomethane are similar to the properties of methane from fossil fuels. With high energy densities and other fuel properties, biomethane is competent, but there are certain environmental constraints that cannot be overlooked when using biomethane as a biofuel. This highlights the need for some serious efforts to improve the environmental properties of biomethane.

1.10 Aviation Fuel

The requirement for fossil fuel is forecasted to grow 1.3% each year up to 2030, whereas the carbon emission from the transport system would likely increase to 80% (Hari et al. 2015). There have been several studies in the field of gaseous and liquid biofuels that can be used to run the land-based transportation. However, air transportation as a contributor to the exhaust emissions and fuel consumption cannot be ignored. During 2005–2010 the total diesel and jet fuel consumptions were between 5 and 6 million barrels per day. The average cost for jet fuels increased from US \$320 per ton in 2004 to US \$1005 per ton in 2011 (Hari et al. 2015). Aviation biofuels have strongly held on to the industry ever since 2008. The first flight run by Virgin Atlantic was fueled by 20% of biofuel along with jet fuel. Blends, as high as 50–50, have been used so far, and in October 2012, 100% biofuel was used in a flight of Dassault Falcon 20 powered by the National Research Council of Canada.

Aviation fuels comprise of both the jet fuel that is used for the turbine engine and the aviation gasoline used for the piston engines. Out of the two, jet fuel that originates from the crude oil is the dominant one used in most of the large aircrafts. The kerosene fraction of the crude oil is used for the extraction of jet fuel, which distills between the gasoline and the diesel fractions (Nygren et al. 2009). The chemical composition of jet fuels can be specified as roughly 60% paraffin (alkanes), 20% aromatic compounds (monocyclic and polycyclic hydrocarbons), and 20% naphthenes (cycloparaffins or cycloalkanes) (Hileman et al. 2010). Olefins or alkenes occur in jet fuels in trace amounts. Sulfur contained in the jet fuel is present in its molecular form with hydrogen and carbon along with traces of oxygen and nitrogen termed as heterocyclics. This sulfur present in jet fuel has some impacts on the air quality standards and fuel lubricity.

Aviation biofuels can be categorized by its fuel quality, ultralow sulfur jet fuel, and hydrocarbon jet fuels with reduced or zero aromatic compound and fatty acid methyl esters (biodiesel or biokerosene). Another ground of categorizing aviation biofuels can be by feedstocks such as vegetable oil, food wastes, and animal fat. Llamas et al. (2012) used transesterified coconut and palm kernel oils with methanol using homogeneous catalysts that resulted in good yields. The fatty acid methyl esters were subjected to vacuum fractional distillation, and the fractions with low boiling point were blended with two varieties of fossil kerosene, one was hydrotreated cut from atmospheric distillation and a commercial JetA1. Various fuel properties for the two blends were tested such as flash point, viscosity, smoke point, etc. From this study, it was concluded that it is feasible to blend up to 10 vol% coconut and palm kernel biokerosene with commercial JetA1 if there are few relaxations in the quality standards set (Llamas et al. 2012).

Chiaromonti et al. (2014) explored the possible routes for sustainable aviation biofuel production from biomass feedstock through either biochemical or thermochemical processes. The possible option for the industrial paraffinic biofuel production is large, which can diversify from biochemical to thermochemical or hybrid routes. It is reported that ITAKA group in Europe is working to develop sustainable synthetic paraffinic kerosene (SPK), which is regarded as environmentally, economically, and socially viable for production at commercial scale. Thus, attempts are being made to use this biofuel in the current aviation industry in Europe. The pre-processing of waste cooking oil is being investigated to make it compatible for standard hydroprocessing including esterification and thermal-catalytic processing at pilot scale. In this study, the initial samples of feedstock oils were characterized to further investigate the conversion of these oils to biokerosene through hydrotreatment route (Chiaromonti et al. 2014).

In the past decade, the fate of aviation biofuel has transformed from an uncertain alternative to a testified and fully certified sustainable alternative for commercial use in 50% blends with the jet fuel. Regardless of the constant efforts and success stories, aviation biofuels have to go a long way to be widely commercialized. Gegg et al. (2014) reviewed the concerns of leading global aviation biofuel industries along with the identification and examination of the factors that dictate the aviation biofuel market globally. Though the future of aviation biofuel seems promising, the way to its commercialization is constrained due to high production costs, limited feedstock and biomass availability, lack of national and international policy support through political sources, and the uncertainties that surround the sustainable production of aviation biofuel at a commercial level. Furthermore, the requirements for establishing a global market to support the commercial production of aviation biofuel is discussed (Gegg et al. 2014). This calls for an international effort to produce and commercialize the use of biofuel in the aviation industry.

1.11 Conclusions

The utilization of biomass as an energy source is becoming essential to alleviate the global warming caused by burning fossil fuels. Environmental concerns such as global warming and climatic changes and the diminishing oil resources and its increasing prices make it essential to explore all kinds of possible biofuels that are sustainable and environment-friendly. The modern era is witnessing a revolution in the energy sector with the advanced processing of the alternative fuel sources. Biofuels from biomass are commonly discussed since a long time and are widely being explored, be it ethanol, butanol, bio-oil, hydrogen, biomethane, biodiesel, or aviation biofuel. However, there are a few limitations over the sustainability of these biofuels. Two of these major limitations are the availability of the feedstock for a mass production of the biofuel at a commercial level to meet global energy demand and the efficient use of the energy derived from these biofuels which need to be transformed from theoretical predictions to practical yields.

The continued use of fossil fuels to meet the increasing energy demands poses a threat to the atmosphere due to increased greenhouse gas emissions and concerns related to the global warming. Additionally, the finite petroleum reserves are depleting and are becoming more expensive. Thus, the economic, environmental, and political limitations are driving the interest in exploring biofuels. Biofuel, a collective term, used for liquid and gaseous fuel sources are primarily derived from biomass through many thermochemical and biochemical pathways.

The reasons for using biofuels are realized to address the global environmental concerns due to greenhouse gas emission, nitrous oxides and volatiles that the fossil fuels release into the environment. However, there are serious sustainability issues related to the use of the liquid biofuels such as ethanol and biodiesel. The feedstock that is used for the production of these liquid biofuels majorly comes from agricultural material (first-generation feedstocks) that competes with the food demands of the world. However, second-generation (lignocellulosic materials) and third-generation feedstocks (algae, municipal solid wastes, sewage sludge, etc.) pose no threat to the food supply and are hence sustainable alternatives to produce advanced biofuels.

The rapid alternations in the global energy scenario have brought to light several alternative fuels that have potential to replace the conventional fossil fuels. An alternative to the conventional petroleum-based fuel is biodiesel that is derived from vegetable oils or used or waste cooking oil that contains triglycerides and animal fats. The huge strain on the depleting petroleum sources and their skyrocketing prices have made it essential for the energy industries to explore alternative fuel sources that are environment-friendly and sustainable. These factors have derived the industries to take a keen interest in sources like vegetable oil or waste cooking oil as a substitute for the petroleum-based fuel. Although holding many promises, the liquid and gaseous biofuels in the current day have a questionable existence on the grounds of economic and commercial prospective. Nevertheless, thorough research and development will lead to a better understanding of the production and utilization of these biofuels for a greener and cleaner future.

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