Chapter 3
Renewable Biofuel Resources: Introduction, Production Technologies, Challenges, and Applications

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Abstract Energy from renewable sources is clean and safe to the environment and is an alternative solution to the future. The demand for energy increases as globalization increases, and to meet the current and future energy demand, different countries all over the world need to rapidly expand energy access and energy availability per capita. Further, a continuous use of fossil fuels, which is non-renewable, is depleting it at a fast rate, and its burning is causing accumulation of carbon dioxide in the environment. Countries are very much dependent on imported petroleum, but biofuels are expected to reduce dependency on imported petroleum with its associated political and economic vulnerability, reduce greenhouse gas (GHG) emissions and other pollutants, and revitalize the economy by increasing demand and prices for agricultural products. Various biofuels and biofuel technologies are available to meet energy demands to some extent with zero carbon dioxide (CO_2) emission. So this chapter examines the feasibility of biofuels as a solution to the world's energy crisis and discusses various generations, sources, and production technologies of biofuels with their application and challenges.

Keywords Renewable · Biofuel · Biodiesel · First generation · Second generation · Third generation · Microalgae · Global warming · CO_2 emission

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3.1 Introduction

Fossil fuels like oil, natural gas, and coal are widely used as transportation and machinery energy source due to the fact that they are easily available, have high heating power, and have good quality combustion characteristics. But they are inadequate to fulfil today's most significant requirements of the societies, in particular, from public health perspectives. Fossil fuels are unsustainable, and an excessive use causes environmental issues related to fossil fuel combustion (Razzak et al. 2013). Increasing demands for energy, growing concern surrounding the continued and excessive use of fossil fuels and depletion of fossil fuel reserves, climate change, rising prices of crude oil, and environmental degradation have forced governments, policymakers, scientists, and researchers for alternative and neutral source of energy (Souza et al. 2017; Chandel et al. 2020). The widespread application of conventional energy resources has contributed to serious challenges, including global warming and climate change by greenhouse gases (GHGs) like carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons (Kiran et al. 2014). These adverse impacts have overshadowed the previous justifications used, including burgeoning petroleum prices, and finite nature of fossil fuel, which have encouraged government and non-government agencies to find environmentally friendly, renewable, and sustainable energy resources for transportation, heating, and electricity generation (Nikolić et al. 2016). Biofuels are liquid fuels that are produced from biomass of plants, animals, and algae and are used for transport or burning purposes. Biofuels are referred to as the future fuel, and the idea was first developed by Rudolph Diesel in the late nineteenth century, and it was run by peanut oil at the Paris Exposition in the year 1900 (Ghobadian et al. 2009). From here it was established that a high temperature of diesel engine is able to run on variety of vegetable oils (Atabani et al. 2011).

Biofuels are produced from the fermentation of biological feedstocks, containing fermentable sugar, carbohydrates, or lipids. This is done by converting biomass of the feedstocks into different forms of energy such as heat, electricity, biogas, and liquid fuels. Global warming is increasing alarmingly, so to reduce global warming, biofuel production should be increased from 9.7×106 GJ d-1 to 4.6×107 GJ d-1 between 2016 and 2040 (Correa et al. 2019). Biofuels are classified into first, second, third, and fourth generations. The aim of biofuel generations is to meet the global energy demand with minimizing environmental impacts.

Complete substitution of petroleum-derived fuels by biofuel is impossible. A marginal replacement of diesel by biofuel can prolong the depletion of petroleum resources and slow down the climate change caused by automotive pollutants. Further, energy security has become a growing concern because the world's energy needs are growing with rising income levels and a growing population. So the energy security and the climate change are the two major driving forces for worldwide biofuel development. This chapter discusses about various biofuels, biofuel technologies of four generations of biofuels, challenges, and opportunities.

3.2 Biofuels

Biofuels are solid, liquid, or gaseous fuel derived from organic matter of plants, animals, and algae. The main difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels from 10% to 45%, while petroleum has essentially none making the chemical properties of biofuels very different from petroleum (Demirbas 2008). Biomass can be converted into liquid and gaseous fuels through various thermochemical and biological processes. Biofuel is a non-polluting, locally available, accessible, sustainable, and reliable fuel obtained from renewable sources (Vasudevan et al. 2005). Biofuels are classified into two categories: primary and secondary biofuels. Primary biofuels are the natural biofuels that are obtained directly from firewood, plants, forest, animal waste, and crop residue. The secondary biofuels are directly generated from plants and microorganisms and may be further divided into three generations (Fig. 3.1). The first-generation biofuels are limited to ethanol, produced from corn and distiller grains, while the second-generation biofuels are produced from lignocellulosic biomass or non-food residues such as agricultural biomass and forestry refuse, as well as energy crops, and the third-generation biofuels are produced from algae, municipal solid wastes, and sewage sludge (Nanda et al. 2018). The fourth-generation biofuels are also reported, which are from genetically modified algae or specially created plant or biomass.

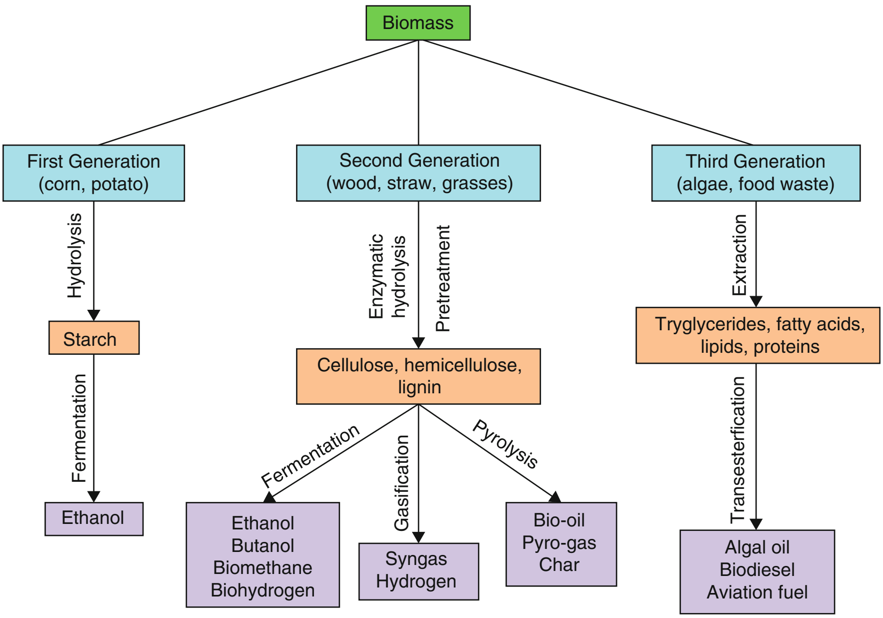

Fig. 3.1 Various generation of biofuels. (Source: Recent Advancements in Biofuels and Bioenergy Utilization. https://doi.org/10.1007/978-981-13-1307-3_1)

3.2.1 *Classification of Biofuel*

3.2.1.1 First-Generation Biofuels

The first-generation biofuels are conventional biofuels, made from sugar, starch, or vegetable oil. They are produced through fermentation, distillation, and transesterification. Sugars and starch are fermented to produce mainly ethanol, while butanol and propanol in smaller quantities. The main advantage of ethanol is that it burns cleaner and therefore produces less greenhouse gases. Another first-generation biofuel, called biodiesel, is produced when animal fat or plant oil goes through a process called transesterification.

One of the main disadvantages of first-generation biofuel is their unsustainable production. It is mostly derived from agricultural resources such as starch, sugar, animal fats, and vegetable oil, which, in turn, has an adverse effect on food production. Furthermore, it threatens our food supply and increases carbon emissions due to the intense growth requirements when planted outside traditional agricultural settings (First Generation Biofuels 2010). Oil is extracted from the crops in the form of biodiesel or bioethanol, which is obtained through fermentation (United Nations Report 2007).

3.2.1.2 Second-Generation Biofuel

The second-generation biofuels overcome the problems associated with the first-generation biofuels. Problems can be solved by the production of biofuels manufactured from agricultural and forest residues and from non-food crop feedstock (Ralph et al. 2009). The second-generation biofuels are produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes. The biomass sources for the second-generation biofuels are wood, organic waste, food waste, and specific biomass crops. Unlike the first-generation biofuel, the second-generation biofuels can be produced by using any plant component as feedstock, like it may be waste material or inedible parts of plant.

3.2.1.3 Third-Generation Biofuel

The third-generation biofuels are related to algal biomass. Due to the limitations of the first-and second-generation biofuels, the need for an alternative feedstock for biofuel production leads to the discovery of the microalgal potential. The feedstocks of the third-generation biofuels are algal biomass such as microalgae, and they have a high lipid productivity. The advantage of microalgae is that they have a high growth rate and can be harvested in only 5–6 days of cultivation. The cultivation of microalgae is environmentally friendly; it requires only a small cultivation area and produces high oil content, oxygen, and hydrogen (Chia et al. 2018; Khoo et al.

2019). Further, the third generation of biofuels is more energy dense than the first and second generation of biofuels per area of harvest. They are low-cost, high-energy, and completely renewable sources of energy.

3.2.1.4 Fourth-Generation Biofuel

The feedstocks of the fourth-generation biofuels are from genetically modified microalgae. These microorganisms are genetically modified to increase the intake of CO_2 for photosynthesis, creating an artificial carbon sink, and to enhance the production of biofuel. Many algal strains (e.g., *Chlamydomonas reinhardtii* sp., *Phaeodactylum tricornutum* sp., and *Thalassiosira pseudonana* sp.) have been genetically modified to increase the growth rate and adaptability to grow in poor nutrient environments (Abdullah et al. 2019).

Further, the fourth-generation biofuels are made by using specially created plants or biomass that have smaller barriers to cellulosic breakdown or they have greater yields. They can be developed on land and water bodies that are unfit for agriculture, so there is no destruction of biomass that takes place. To be considered as an alternative fuel and suitable substitute for fossil fuel, it should possess greater environmental benefits over its previous generation of biofuels and should be cost effective, and production will be in sufficient amounts to have a meaningful impact on energy demands. One of the most important aspects is that the net energy derived from the feedstock should exceed the amount that is required for production. In recent years, scientists have designed eucalyptus trees (Olaganathan et al. 2014) that are able to accumulate three times more CO_2, reduce greenhouse gases, and prevent global warming. Mankind bids to reduce greenhouse gases and salvage the current state of global warming.

3.3 Sources of Biofuel and Bioenergy

3.3.1 Nonedible Vegetable Oils

Biofuel production using edible oils as a feedstock has certain limitations with respect to their cost and source from which they are derived. So to address this issue, there is a need of less expensive feedstocks. Nonedible oils have a great capability to be used as feedstocks for biofuel production particularly biodiesel (Rasool and Hemalatha 2016). Nonedible oils as feedstocks for biodiesel production can help in reducing the cost of biodiesel production. Jatropha, *Pongamia*, palm, mahua, etc. are the various sources that are present in nature in excess amounts and can serve as a great feedstock. When compared to edible oils, these plants are very economical and are readily available in developing countries. For example, the seeds of mahua (*Madhuca indica* J. F. Gmel.) have about 30%–40% of oil content known as mahua oil. Jatropha (*Jatropha curcas* L.), which grows well in marginal or poor soils, is a drought-resistant and semi-evergreen shrub producing seeds that contain around 37% oil. The oil derived from Jatropha seeds, commonly known as Jatropha oil, can be straight away used as a fuel without the process of refining. As a fuel, Jatropha oil has been successfully tested for a simple diesel engine and it burns with a clear, smoke-free flame. Another example is Karanja [*Millettia pinnata* (L.) Panigrahi]. Neem (*Melia azadirachta* L.) belongs to the Meliaceae family. The seed kernels of neem tree have a good content of fat (ranges from 33% to 45%).

Biodiesel produced from nonedible vegetable oil is a good alternative for diesel fuel (Demirbas et al. 2016). The use of nonedible plant oils is more significant compared with edible plant oils because of the tremendous demand for edible oils as food, and they are too expensive to be used as fuel at present (Mahanta et al. 2006).

Nonedible oil plants can be easily grown in wastelands that are not useful for food crops, and their cost of cultivation is much lower, and these plants can sustain reasonably high yield without extra care. Nonedible oil plants are well adapted to arid and semi-arid conditions and require low fertility and moisture demand to grow (Atabani et al. 2013).

3.3.2 Edible Vegetable Oils

Edible oils have a great potential to be used as a feedstock for the production of biofuels. Palm oil, soybean oil, and rapeseed oil represent the main edible oils that are produced worldwide, and together they constitute 75% of the total edible oil production in recent times. Edible vegetable oils as raw materials for the first-generation biodiesel are a major concern. There are many things that need to be taken into consideration for biofuel production by using edible oils as a raw materials like the source of the oil used for biofuel production, i.e., whether food or non-food crops are used to derive that oil, the oil composition, and how well it can serve the purpose of using it as a feedstock. There is a limitation on the way of edible oils as feedstocks because it raises the food-versus-fuel debate that may cause high food prices, particularly in developing countries. It can cause environmental problems due to the use of a wide area of arable land available. This problem can create serious ecological imbalances as countries worldwide convert forests to farmland by deforestation (Negm et al. 2017). Therefore, nonedible vegetable oil or second-generation raw materials have become more attractive for the production of biodiesel.

3.3.3 Monocot Plant

Monocots are those plants that have a single cotyledon. Monocot plants like corn, maize, wheat, sugarcane, sorghum, miscanthus, etc. are used as a source of bioenergy (Rasool and Hemalatha 2016). The conversion of corn to ethanol takes place by the process of fermentation. Maize is one of the largest crops that is cultivated worldwide, and it has the property of playing an important role in biofuel development. If maize are used for the production of biofuels, then it needs to be cultivated for two purposes, viz., for grain production and for stem biomass production in higher yields. Maize can be cultivated as a dual crop with ease because of the availability of resources such as those of agronomic and genomic resources. Sugarcane is effective crops in the collection of solar energy and its conversion to chemical energy. The potential of sugarcane as a biomass feedstock is widely acknowledged. When sugarcane is given for processing, there is the production of sugarcane bagasse in large amount, which is nowadays used for steam and electricity generation by burning in boilers. Wheat has the potential to become a major biofuel crop. Wheat after fermentation produces ethanol as a fuel that can be used to run vehicles.

3.3.4 Algae

Microalgae are unicellular or simple multicellular organisms. They can be prokaryotic or eukaryotic in nature and have the ability to grow naturally in fresh- or saltwaters. Due to the cellular structure of microalgae, they can easily and efficiently convert solar energy. Microalgae are the oldest living organisms on the earth, and they can grow at a very fast rate and have ability to double their biomass per day (Song et al. 2008). Among the many species of microalgae, there are some species having an oil content of about 80%. Microalgae can produce higher amounts of lipids in comparison with palm oil and soybean (Htet et al. 2013). The common microalgal species are *Chlorella* sp., *Botryococcus* sp., and Scenedesmus sp., and they are easy to cultivate in comparison to other species and potentially contain more lipids (Pokoo-Aikins et al. 2009; Lee et al. 2010). *Chlorella* spp. specifically *C. emersonii*, *C. minutissima*, *C. vulgaris*, and *C. protothecoides* were capable of producing 63% lipid content on a dry biomass basis (Song et al. 2008). The biodiesel produced from these species are acid methyl ester, linoleic acid methyl ester, and oleic acid methyl ester. The third-generation biofuels, i.e., algal biofuels, have five different possible pathways for the algae-to-biofuel production. They are open pond system, hybrid system, modular closed photobioreactor, heterotrophic fermentation, and integrated cultivated system (Olaganathan et al. 2014). Microalgae have various advantages in CO_2 capture, bio-oil generation, photosynthetic conversion efficiencies, rapid rate of biomass production, and their year-round harvest (Demirbas et al. 2011).

Algae produce a wide variety of biofuel feedstock and they have the ability to grow and develop in diverse ecosystems. Algae have distinguished environmental bioremediation such as CO_2 fixation from the atmosphere and reduce and mitigate industrial greenhouse gases such as carbon dioxide, contributing to carbon balance and also responsible for water purification. The main advantage of algae is that they don’t require land to grow, so there is no competition with crops and the food market (Chisti 2007; Wang et al. 2008). Microalgal biodiesel comes under the third generation of biofuels. Microalgal biofuels can help in overcoming the limitations of the first and second generation of biofuels (Saifullah et al. 2014).

3.3.5 Animal Fat

The main issue that comes in the way of biodiesel production is the choice of feedstocks. In recent times, inedible animal fats are gaining a lot of interest as the source of lipids. Animal fats can be utilized as easily available biofuel feedstocks. Animal fats as biofuel feedstocks serve two purposes, viz., their need for disposal as waste gets eliminated and they also contribute for biodiesel production. Biodiesel, which is derived from soybean oil, is more resistant to cold weather when compared to the biodiesel derived from animal fat. Biodiesel from animal fat reduces 80% fossil CO_2 reduction in comparison to 30% for soybean. Feedstock from animal waste fats are obtained from tanneries, slaughter houses, and meat processing units, and they are considered as potential feedstock for biodiesel production because of its better calorific value, chemical inertness, zero corrosivity, and good renewable resources. Among these sources, leather tanneries produce 55% of solid wastes during trimming, prefleshing, fleshing, and shaving operations, which majorly consist of subcutaneous fat wastes. Waste animal fat not only reduces the solid waste disposal but also reduces the overall production cost of biodiesel.

3.4 Biofuel Production Technologies

The basic technologies used for converting crude vegetable oil and/animal fat that can be made into biofuel for diesel engines are:

- Thermal cracking or pyrolysis.
- Microemulsion.
- Direct use or blending of oils.
- Transesterification reaction.

3.4.1 Pyrolysis

Pyrolysis includes chemical transformation with the help of thermal energy in the absence of air or oxygen or by the use of heat and catalyst, which results breaking of bonds and construction of tiny molecules. Pyrolysis is conducted at a temperature range of 400–600 °C. Depending on the rate of pyrolysis, there is a formation of gases, bio-oil, and char. The pyrolysis process classifies into three subclasses:

Table 3.1 Classification of pyrolysis methods with differences in temperature, residence time, heating rate, and major products

Method	Temperature (°C)	Residence time	Heating rate (°C/s)	Major products
Conventional/slow pyrolysis	Med–high (400–500)	Long 5–30 min	Low 10	Gases Char Bio-oil (tar)
Fast pyrolysis	Med–high (400–650)	Short 0.5–2 s	High 100	Bio-oil (thinner) Gases Char
Ultrafast/flash pyrolysis	High (700–1000)	Very short <0.5 s	Low 10	Gases Bio-oil

conventional pyrolysis, flash pyrolysis, and fast pyrolysis (Czernik and Bridgwater 2004) as mentioned in Table 3.1.

The chemical compositions (heavy hydrocarbons) of the diesel fractions produced by catalytic cracking of copra oil and palm oil are similar to fossil fuels (Ma and Hanna 1999). The process was easy and operative as compared with other cracking processes according to them. The pyrolyzate (product of pyrolysis) has lower viscosity, flash point, and pour point than petroleum diesel fuel and equivalent calorific values (Mahanta and Shrivastava 2004). In addition, the cetane number of the pyrolyzate is lower. The thermal pyrolysis of triglycerides has several advantages such as lower processing cost, simplicity, less waste, and no pollution (Singh and Dipti 2010).

3.4.2 Microemulsification

This method includes dispersion of surfactant, water, and oil, which is an isotropic and thermodynamically constant system with diameter range 1–100 nm (Slomkowski et al. 2011).

The biodiesel microemulsion incorporates diesel fuel, vegetable oil, liquor, surfactant, and cetane improver in reasonable extents. The higher alcohols are utilized as surfactants and alkyl nitrates are utilized as cetane improvers (Chiaramonti et al. 2003). All microemulsions having butanol, octanol, and hexanol possess the highest viscosity required in diesel fuel. In micellar solubilization of CH_3OH in triolein and soybean oil, the 2-octanol is a viable amphiphile (Schwab et al. 1987). In spite of the lesser cetane number and energy, the working of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil is compactable with NO_2 diesel fuel (Srivastava and Prasad 2000). NO_2 diesel fuel is a fuel with distillation temperature of 640° Fahrenheit at the 90% recovery point and meets the specifications defined in ASTM Specification D 975 (Bart et al. 2010). The microemulsified diesel causes problems like injector needle sticking, carbon deposit formation, and incomplete combustion in engine when used continuously (Pairiawi 2010).

3.4.3 Dilution/Blending

Direct uses of vegetable oils are not satisfactory and impractical for both types of diesel engines. The main problems with blending are the presence of free fatty acid (FFA), high viscosity, carbon deposits, lubricating oil thickening, and oxidation and polymerization during storage and incomplete combustion (Ma and Hanna 1999). In such cases, it is helpful to dilute vegetable oils with diesel, solvent, or ethanol. Blending reduces viscosity and density of plant oils. The thermal efficiency, brake torque, and power will increase by adding 4% ethanol in diesel (Bilgin et al. 2002).

In their review of biodiesel production methods, Ma et al. (Ma and Hanna 1999) mentioned that the viscosities of 50/50 (winter rapeseed oil and diesel) and 70/30 (whole winter rapeseed oil and diesel) blends were much higher (6–18 times) than NO_2 diesel.

3.4.4 Transesterification

Transesterification is the main convenient process for preparation of biodiesel from oil and fat, which chemically resembles petroleum diesel. Through this method, oils and fats (triglycerides) are converted to their alkyl esters with reduced viscosity to near diesel fuel levels. The simplest chemical reaction for transesterification of triglycerides is presented in (Fig. 3.2). There is a different way to produce biodiesel through transesterification, which is shown in Fig. 3.3.

All of the catalytic transesterification processes involve the reaction of a triglyceride (fat or oil) with an alcohol in the presence of some catalyst to form esters and glycerol. The nature of the fatty acids can, in turn, affect the characteristics of the biodiesel (Lokanatham 2013). A successful transesterification reaction for efficient biodiesel production is signified by easy and effective separation of the ester and

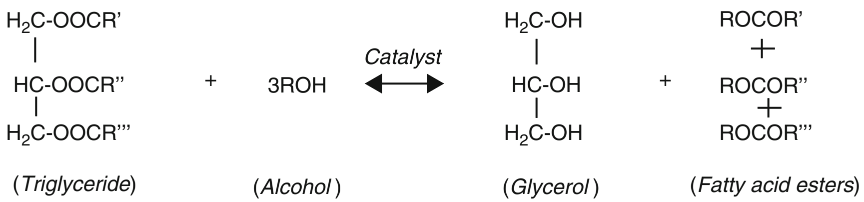

Fig. 3.2 The general chemical reaction depicting transesterification of triglycerides (Koh and Mohd. Ghazi 2011)

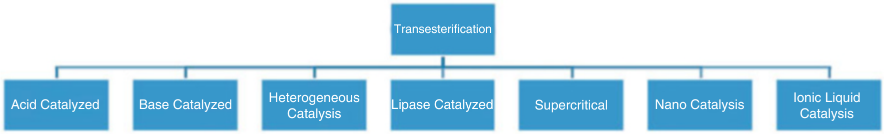

Fig. 3.3 Schematic depicting major transesterification process types

glycerol layer after the reaction time. The heavier, co-product glycerol can be purified for use in other industries, e.g., pharmaceutical, cosmetics, etc.

3.4.4.1 Homogeneous Acid-Catalyzed Transesterification

Acid-catalyzed transesterification was the first method to produce biodiesel (ethyl ester) from palm, ethanol, and sulfuric acid (Knothe et al. 2005). There is a reaction of a triglyceride (fat/oil) with an alcohol in the presence of acid catalyst to form esters (biodiesel) and glycerol. But this requires a longer reaction time and a higher temperature than the alkali-catalyzed reaction (Zhang et al. 2003).

Acid-catalyzed transesterification starts by mixing the oil directly with the acidified alcohol acting both as a solvent and as an esterification reagent. The reaction should be carried out in the absence of water, in order to avoid the formation of carboxylic acids, which reduce the yields of alkyl esters (Mahanta and Shrivastava 2004).

The study shows the rate of esterification of oleic acid significantly decreased as the initial water content increased to 20% of the oil (Park et al. 2010). Sulfuric acid, sulfonic acid, and hydrochloric acid are the usual acid catalysts, but the most commonly used is sulfuric acid. There are also various studies done to see the yield effect of using alternative acids. The $AlCl_3$ could be used to catalyze the esterification of stearic acid suggesting that it is a potential alternative catalyst for biodiesel preparation using cheaper vegetable oil containing high amounts of FFA (Soriano Jr et al. 2009).

3.4.4.2 Homogeneous Alkaline-Catalyzed Transesterification

The alkaline-catalyzed transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of alkaline catalysts such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates to form esters (biodiesel) and glycerol. Alkali-catalyzed transesterification is much faster and less corrosive to industrial equipment than acid-catalyzed transesterification and therefore is the most often used commercially (Ranganathan et al. 2008; Marchetti et al. 2007).

The main disadvantage that resulted due to saponification reaction is the consumption of catalyst and increased difficulty in separation process, which leads to

Table 3.2 Comparison of different types of catalysts used in the transesterification of used frying oil (temperature at 70 °C, reaction time 30 min, and methanol-to-oil molar ratio of 7.5:1) (Leung and Guo 2006)

Catalyst	Concentration of the catalyst (wt.%, by weight of crude oil)	Ester content (wt.%)	Product yield (wt.%)
NaOH	1.1	94.0	85.3
KOH	1.5	92.5	86.0
CH_3ONa	1.3	92.8	89.0

high production cost. In addition to that, formation of water in the product will also inhibit the reaction (Díaz et al. 2014).

The efficient production of biodiesel using base-catalyzed transesterification is not only dependent on the quality of the feedstock; it is also dependent on the crucial reaction operation variables such as alcohol-to-oil molar ratio, reaction temperature, rate of mixing, reaction time, type and concentration of catalyst, and also the type of alcohol used (Leung et al. 2010; Singh and Dipti 2010; Fadhil and Ali 2013).

The catalysts usually used in base-catalyzed transesterification are sodium hydroxide, potassium hydroxide, and sodium methoxide. Sodium hydroxide is mostly preferable owing to its intermediate catalytic activity and a much lower cost (Atadashi et al. 2013). The result of their study is shown in Table 3.2.

This study revealed that sodium hydroxide is better in attaining purity percentage (ester content) than the others, whereas sodium methoxide is good in providing a higher yield percentage.

3.4.4.3 Heterogeneous-Catalyzed Transesterification

The heterogeneous catalysts are usually solid base catalysts that have various advantages, such as having mild reaction condition, easy separation, and high activity and less contaminant (Jagadale 2012). The heterogeneous catalyst offers high selectivity and reusability characteristics (Baskar and Aiswarya 2016).

Heterogeneous solid catalysts show the ability to simultaneously catalyze esterification and transesterification reactions (Borges and Díaz 2012). Heterogeneous catalysts such as amorphous zirconia, titanium, and potassium zirconias have also been used for catalyzing the transesterification of vegetable oils: the amorphous zirconia catalysts, titanium-, aluminum-, and potassium-doped zirconias, in the transesterification of soybean oil with methanol at 250 °C and the esterification of n-octanoic acid with methanol at 175–200 °C (Furuta et al. 2006). We can also prepare biodiesel from *Jatropha curcas* oil catalyzed by solid super base of calcium oxide (Zhu et al. 2006). The heterogeneous acid catalyst also simplifies product separation and purification and reduces waste generation (Melero et al. 2009). Solid acid catalysts can be recycled and easily removed and can simultaneously catalyze esterification and transesterification (Peng et al. 2008).

3.4.4.4 Lipase-Catalyzed Transesterification

The other way of transesterification of oils and fats for biodiesel production is using enzymes in which there is no problem of saponification, purification, washing, and neutralization so that it is always a preferred method from these perspectives. Enzymatic catalysts can also be applied on a feedstock with high FFA and can convert more of the oil into biodiesel. However, the problems associated with enzymatic catalysts are their higher cost and longer reaction time (Leung et al. 2010).

Usually because of these two drawbacks, enzyme-catalyzed transesterification method is not very frequently used. The enzymatic transesterification produces high purity product (esters) and enables easy separation from the by-product, glycerol (Ranganathan et al. 2008; Devanesan et al. 2007). The enzymes that are usually found to be capable of catalyzing transesterification are the lipases.

The most desirable characteristics of lipases for transesterification of oils for biodiesel production are utilization of all mono-, di-, and triglycerides and the free fatty acids, low product inhibition, high activity and yield in non-aqueous media, low reaction time, reusability of immobilized enzyme, and temperature and alcohol resistance (Bajaj et al. 2010). There is extracellular lipase as a catalyst for recovery, purification, and immobilization processes for industrial application (Ban et al. 2001).

The enzyme (both intracellular and extracellular) should be reused by immobilizing in a suitable support particle to reduce cost of production (Pairiawi 2010). Nanoparticles strongly influence the mechanical properties of the material like stiffness and elasticity and provide biocompatible environments for enzymatic immobilization (Meryam Sardar 2015). The use of lipase is a great viable method for the production of ester from different sources of oil or grease even (Marchetti et al. 2007).

3.4.4.5 Nanocatalyzed Transesterification

There a number of recent developments in catalytic conversion of oils and fats to biodiesel. Among them, biodiesel production using nanocatalyst and ionic liquid catalysts is more promising in terms of a few advantages over the conventional acid/base catalysts. Nanocatalysis involves the use of nanomaterials as catalysts for a variety of homogeneous and heterogeneous catalysis applications. Nanoscale catalysts have high specific surface area and surface energy, resulting in high catalytic activity. Generally, nanocatalysts improve the selectivity of the reactions by allowing reaction at a lower temperature, reducing the occurrence of side reactions, higher recycling rates, and recovery of energy consumption (Sharma et al. 2015). In this respect, nanocatalysts are promising alternatives for efficient production of biodiesel from oils and fats as they have high specific surface area and high catalytic activities, eliminating the specific problem of mass transfer resistance associated with conventional catalysts (Table 3.3).

Table 3.3 Summary of some optimized productions of biodiesel from different feedstock types through transesterification using nanocatalysts

Feedstock	Alcohol	Alcohol-to-oil ratios	Nanocatalyst	wt.% of catalyst	Temp. (°C)	Reaction time	Yield %
Waste mixed vegetable oil	Methanol	5:1	Smoke deposited nanosized MgO	1.5	55	45 min	98.7
Stillingia oil	Methanol	12:1	$KF/CaO–Fe_3O_4$ (calcinated at 600 °C)	4	65	3 h	95
Chinese tallow seed oil	Methanol	12:1	KF/CaO	4	65	2.5 h	96.8
Waste cooking oil		7:1	Nano CaO	1.5	75	6 h	94.37
Waste cooking oil		7:1	Mixture of nano CaO and nano MgO	3	75	6 h	98.95
Soybean oil		12:1	Nanoparticle of CaO from calcium nitrate (CaO/CaN)	8	65	6 h	93

The solid base nanocatalyst KF/CaO can be used for biodiesel production with a yield of more than 96% (Wen et al. 2010). This catalyst can efficiently be used to convert the oil with a higher acid value into biodiesel (Wen et al. 2010; Chaturvedi et al. 2012). There is a comprehensive study of smoke deposited nanosized MgO as a catalyst for biodiesel production. They studied the transesterification reaction to determine the optimum conditions for different parameters like catalyst quantity, methanol-to-oil molar ratio, reaction temperature, and reaction time (Sivakumar et al. 2013). The nanocatalyst from snail shell has excellent catalytic activity and stability for the transesterification reaction, which is potentially used as a solid base nanocatalyst for biodiesel production (Gupta and Agarwal 2016). The catalytic activity of such nanocatalysts is usually affected by calcination temperature during catalyst preparation with calcination (Hu et al. 2011).

3.4.4.6 Transesterification Using Ionic Liquids as Catalysts

Ionic liquids are organic salts comprising anions and cations that are liquid at room temperature. The cations are responsible for the physical properties of ionic liquids (such as melting point, viscosity, and density), while the anion controls its chemical properties and reactivity (Earle et al. 2009). Their unique advantage is that while being synthesized, they can be moderated to suit the required reaction conditions.

Another great advantage of ionic liquid−catalyzed transesterification for biodiesel production is the formation of a biphasic system at the end of the reaction. This biphasic system occurs because the ionic liquid, insoluble in the organic phase, remains in the aqueous phase along with alcohol, the catalyst used, and the glycerol produced during the reaction (Gamba et al. 2008). This makes it very easy to separate the final products. Pure biodiesel can then be isolated by simple vacuum evacuating of this very little amount of methanol. The most widely studied and discussed compounds ionic liquids for catalysis of transesterification reaction are 1-n-butyl-3-methylimidazolium cation (Andreani and Rocha 2012). The ionic liquid has good reusability and can be easily separated from the biodiesel by simple decantation (Guo et al. 2014).

Supercritical Transesterification

One of the approaches to overcome problems associated with poor immiscibility between the reactants is to use supercritical method. Supercritical alcohol transesterification reaction takes place under extremely high temperature and pressure. In the supercritical transesterification method, methanol and oil will form a homogenous fluid. This is due to the sharp drop in the solubility of methanol and reduction in dielectric constant, which makes methanol a non-polar substance (Leung et al. 2010). When we consider specific application of the mothed for biodiesel production, supercritical methanol is usually used to speed up the transesterification reaction. Using this technique, the conversion of vegetable oils into biodiesel is done in about 4 min, but extremely high pressure and temperature are required for this method, which makes it highly sensitive and costly (Shahid and Younis 2011). A lot of energy is required to build such a high pressure and temperature. Some authors recommend the use of co-solvent to improve the conversion efficiency.

In general, the supercritical methanol process, which is non-catalytic, is simpler in purification and takes lower reaction time and lower energy use than the common commercial process (Kusdiana and Saka 2004; Leung and Guo 2006). It produces more than a kilo of fuel per kilo of oils used (Marchetti et al. 2008). Van Kasteren and Nisworo (2007) have proved this by using one reaction step in the process and propane as a co-solvent in supercritical biodiesel production plant so as to decrease operating cost.

Similarly, Marulanda (2012) carried out a lab-scale experiment on biodiesel production process by supercritical transesterification in a continuous reactor working at a 9:1 methanol-to-triglyceride molar ratio and 400 °C. Different studies done on investigation of optimum condition for supercritical transesterification process agree that among the determinant variables, temperature has the highest impact on yields, followed by reaction time and pressure. Kiss et al. (2014) have done a series of experiments with ethyl alcohol to the effect of temperature, time, and pressure. They found that by increasing the reaction time at 350 °C and 12 MPa, yield increases during the whole range (from 63.36% to 93.22%).

3.5 Applications of Biofuels

3.5.1 *Transportation*

More than 30% of the energy is used in the United States for vehicle transportation. Transport worldwide accounts for 24% of energy and over 60% of absorbed oil, and this means that more than one-third of the oil is used for driving the vehicle. The main problem with alternative energy is that sun, wind, and other alternative energy are not practical for transportation. Researcher believe that effective breakthroughs in practical technology development are still underway. The biofuels can be converted to hydrogen vapors used in adjacent fuel cells. Major car brands have already invested in stations for biofuel-driven vehicles. Transportation and agricultural sector are two of the major consumers of fossil fuels and the biggest contributor to environmental pollution, which can be reduced by replacing mineral-based fuels with bio-origin renewable fuels (Sheehan John et al. 2012).

3.5.2 *Power Generation*

The fuel cells have power generation applications that can be used as electricity (Sahin 2011). Biofuels can be used to produce electricity in backup systems where emissions are the most important. This facility is included in schools, hospitals, and other forms located in residential areas. The United Kingdom is the largest market for biofuel-to-electricity generation, generating enough power for 350,000 households from landfill gas alone.

3.5.3 *Provide or Generate Heat*

Over the last few years, bioheat has grown. With the main use of natural gas coming from fossil fuels, heat from hydro-crushing will increase the production of natural gas. Natural gas does not only come from fossil materials, but it can also come from recently grown materials. Most of the biofuels used for heating are significant. Houses use wooden stoves, not gas or electricity, because wood is the most practical and useful way to heat. Biodiesel mixing reduces emissions of nitrogen and sulfur dioxide (McCarthy et al. 2011).

3.5.4 Charging Electronics

According to scientists at Saint Louis University, fuel cells produce electricity by cooking oil and sugar. Consumers can use these instead of generating electricity. Consumers can charge their cell phones from their computers using fuel cells instead of batteries. Although they are still in development, the fuel cells have the potential to become a source of prepared power.

3.5.5 Clean Oil Spills and Grease

Biofuels are known to be environmentally friendly and can help with oil spills and oil removal. The oil has been tested to work as their potential detergent in areas contaminated with water. The results have been found to increase the area of recovery and allow it to be removed from the water. Biofuels can be used as industrial solvents for the cleaning of metals, which is also beneficial because they have fewer toxic effects.

3.6 Advantages of Biofuels

3.6.1 Economic Fuel with Cost-Benefits

As compared to fossil diesel, biofuel is made from renewable resources and relatively less-flammable materials. It produces less harmful carbon emission compared to diesel. Biofuels can be created from a wide range of materials, and it has significantly better lubricating properties. Vehicles that run on biodiesel get 30% better economy than gasoline-powered vehicles, which saves drivers money every time they visit the gas station (Volkswagen Group 2010). Previous results showed that some of the biodiesel buses created less pollution.

The cost of biofuels and gasoline is the same in the market. However, the overall cost-benefit of using them is much higher. Biofuels are cleaner fuels; they produce fewer emissions on burning. With the increased demand for biofuels, they have the potential of becoming cheaper in the future. According to the RFA February 2019 Ethanol Industry Outlook report, "Ethanol remains the highest-octane, lowest-cost motor fuel on the planet. It aims to make it possible for somebody to high-value products from biomass or waste resources" and reduce the cost of producing biopower (Renewable Fuels Association 2008). So, the use of biofuels will be less of a drain on the wallet.

3.6.2 High-Quality Engine Performance

Biofuels are suitable to current engine designs and perform are very well in most conditions. It has higher cetane and very good lubricating properties. The neat thing about biodiesel is that it can run in existing engines with little or no modification to the engine or its fuel system (Al-Mashhadani and Fernando 2017). Performance is the same. The durability of the engine increases when we used biodiesel as a combustible fuel, and there is no requirement for engine conversion and it keeps the engine running for longer duration, so requires low maintenance, which brings down overall pollution check costs. Engines designed like that to work on biofuels produce less emission than other diesel engines.

3.6.3 Biofuel Refineries Are Cleaner

When oil comes out of the ground, it doesn't magically transform itself into gasoline or home heating oil. Oil refineries must convert crude oil into useable products. There are 153 of these refineries in the United States, and more than a million people live within 30 miles (48.28 km) of them. For the most part, biofuel refineries, which turn feedstock such as corn and soybean into biofuel, are more environmentally friendly. On the other side, ethanol plants fuelled by biomass and biogas produce less gas emissions and are cleaner to run (Oregon Environmental Council 2010).

3.6.4 Easily Available Resources

Gasoline is refined from crude oil, which is obtained from a non-renewable resource; the current reservoirs of gas will sustain, and they will end in the near future. Biofuels are made from many different sources such as manure, waste from crops, other by-products, algae, and plants grown specifically for the fuel (Rodionova et al. 2017). Most of the environmental sources like manure, corn, switchgrass, soybeans, and waste from crops and plants are renewable and are not finished any time soon, and it makes the use of biofuels efficient in nature, and again and again, these crops can be replanted.

3.6.5 Reduces Greenhouse Gases

Global warming is reshaping the planet whether it is in Africa's highest mountain or the overall increase in the levels of the oceans (Bioenergy Task 2007). While some people see global warming as a natural event, most scientists agree that fossil fuels, such as oil and coal, drive the temperature increase. When burned, fossil fuels release greenhouse gases, including carbon dioxide, into the atmosphere. Most people in the world are using biofuels, like ethanol or biodiesel, to power their homes, cars, and factories. Fossil fuels burn and produce large amounts of gases, i.e., carbon dioxide, in the atmosphere. The greenhouse gases absorbed sunlight and cause the planet to warm. The burning of coal and oil increases the temperature and produces global warming (Kline and Dale 2008). To reduce the greenhouse gases, people around the world are using biofuels (Koh and Ghazoul 2008).

3.6.6 Economic Security

Every country has not reserved crude oil. Using it to import the oil puts a huge dent in the economy (Pauw and Thurlow 2010). If large numbers of people start shifting toward biofuels, then the country can reduce its dependence on fossil fuels. Biofuel production increases the demand for suitable biofuel crops, providing a boost to the agricultural industry. From this, more jobs will be created with a growing biofuel industry, which will keep our economy well secured.

3.6.7 Reduce Foreign Oil Dependence

People waited in line for hours to buy what little gasoline there was. Governments tried to find new ways to reduce the energy crisis. Eventually, the oil-producing countries lifted the embargo, but our thirst for oil continued. Today, humans consume 85 million barrels of oil a day. Americans use nearly 18.7 billion barrels a day (Central Intelligence Agency 2010). The locally grown crops have reduced the nation's dependence on fossil fuels, and many experts and scientists believe that it will take a long time to solve our energy needs for country development.

3.6.8 Less Pollution

For its part, ethanol generally burns better and more robustly than gasoline, generating less pollution in the air. As compared with gasoline, an E85 fuel blend (15% ethanol, 85% gasoline) burned in an efficient engine produces fewer toxins, including 40% less carbon dioxide, 20% less particulate matter, and 80% fewer sulfates (Energy Future Coalition 2010). However, scientists at Stanford University in California say ethanol releases many of the same pollutants as gasoline. We know that the biofuels can be made from renewable resources, and they cause less pollution to the planet. This is the reason why use of biofuels is being encouraged.

3.6.9 Health Benefits

Each year in the United States, 10,000 people die from pollution created by gasoline engines (Reilly 2007). Among other irritants and pollutants, gasoline releases nitrogen oxide and acetaldehyde. Acetaldehyde molecules react with sunlight to form smog. These emissions make thousands of people sick every year with respiratory ailments and cancers (Reilly 2007). Biofuels produce fewer toxins into the air than fossil fuels. When compared to diesel, biodiesel reduces smog-forming particulate matter, which reduces cases of asthma and other respiratory illnesses. In addition, biodiesel doesn't emit any sulfur oxides and sulfates, which contribute to acid rain.

3.7 Challenges of Biofuels

All types of benefits are associated with biofuels, but they are slightly expensive to produce in the current market. If the demand increases and to meet the increasing demand, the supply will be a long-term operation, which will be quite expensive than others. Such a disadvantage is still preventing the use of biofuels.

We know that biofuels are produced from crops, and these crops need fertilizers to grow in a better way. The drawback of using fertilizers is that they can have harmful effects on the surrounding environment because fertilizers contain nitrogen and phosphorus and may cause water pollution (Al-Mashhadani and Fernando 2017). They can be washed away from soil to nearby lakes, rivers, or ponds.

Biofuels are extracted from plants and crops that have high levels of sugar. However, most of these crops are also used as food for living things. The waste material from plants can be used as a raw material. It will take up agricultural space from other crops, which can create a lot of problems. Using land for biofuels may not cause an acute shortage of food; however, it will create pressure on the current growth of crops.

The carbon footprint (Tseten et al. 2014) for biofuels is less than the traditional forms of fuel when burnt. However, the process by which they are produced is dependent on lots of water and oil. Large-scale industries that used biofuel are known to emit large amounts of emissions and cause small-scale water pollution. Unless a more efficient means of production is put into place, the overall carbon emission does not get a very big dent in it. It also causes an increase in NOx.

To irrigate the biofuel crops, large quantities of water are required, and it may impose strain on local and regional water resources, if not managed wisely. For the production of corn-based ethanol to meet the local demand for biofuels, large quantities of water are used that could put unsustainable pressure on local water resources.

For the production of biofuels, the current technology being used is not as efficient. Scientists are engaged in developing better ways by which we can extract this fuel. However, the cost of research and future installation shows that the price of biofuels will see a significant spike. The prices are comparable with gasoline and are still feasible. The rising of prices constantly may make the use of biofuels as harsh on the economy as what the rising prices of gas are doing right now.

To grow a biofuel feedstock when the land is used, it has to be cleared of native vegetation, which then leads to damaging the ecology. The first damage is done by destroying local habitat, animal dwellings, and microecosystems and decreasing the overall health of natural resources of the region. The second damage is done in the carbon debt created. This leads to the production of greenhouse gases and puts the region at a net positive, when it is needed to deforest an area and prepare it for farming and to plant the crop. Finally, changing the land to an agricultural status almost always means fertilizers are going to be used to get the most yields per area. The use of biofuel is less suitable in low temperatures. In cold weather, it creates problems due to attraction with moisture than fossil diesel. It also provides atmosphere to increases microbial growth in the engine that clogs the engine filters.

3.8 Environmental Effect of Biofuels

The production of biofuels presents a new economic opportunity for the world, and as a society, we need an action to significantly reduce the world's greenhouse gas (GHG) in the coming decades. The GHG emission is projected to increase fifty percent and will become the fastest growing driver of climate change by 2050, and this is especially in the fastest growing country. A rapid increase in GHG emission is affecting the earth's climate. Accordingly, international energy agency has introduced renewable energy as a possible solution to reduce GHG emission and ensure a stable climate all over the world. The major type of renewable energy (Naikwade et al. 2012) is wind, geothermal, solar, ocean power, hydropower, and biomass. Out of the various renewable energies, biofuels continue to represent the vast majority of the currently developed and consumed renewable energy (Naikwade et al. 2012). Biofuels from some sources can even generate more greenhouse gas emissions than fossil fuels.

Biofuel production can affect agricultural biodiversity through the restoration of degraded lands, but some of its impacts will be negative. In general, wild biodiversity is threatened by the loss of habitat when the area under crop production is expanded, whereas agricultural biodiversity is affected by large-scale monocropping, which is based on a narrow pool of genetic material and can also lead to a reduced use of traditional varieties. The first pathway for biodiversity loss (Tseten et al. 2014) is land conversion for crop production.

Many biofuel crops are well suited for tropical areas. This increases the economic growth in countries with biofuel production potential to convert natural ecosystems into feedstock plantations (e.g., oil palm), causing a loss of wild biodiversity in these areas, while oil palm plantations do not need much fertilizer or pesticide. Most studies show that producing the first-generation biofuels from current feedstocks results in emission reductions in the range of 20−60% relative to fossil fuels, provided the most efficient systems are used and carbon releases deriving from land-use change are excluded. Biofuels affect the environment in all stages of their production and use. Some effects are easily noticed (e.g., odors emanating from an ethanol plant). Other effects are less apparent, including those that result from activities along the biofuel supply chain (e.g., nitrate leaching into the surface waters as a result of nitrogen fertilizer application on corn fields) and those that could occur beyond the supply chain via market-mediated effects (e.g., loss of biodiversity on land-use change induced by higher corn prices). For example, the wide expansion in corn production (first-generation biofuel) has generated potential water stress at regional and local scales because the corn requires more water compared to other crops (e.g., wheat and soybean) due to the additional water consumed in almost every growing stage, especially the joining stage.

3.9 Conclusion

Biofuels are the best alternative to petroleum-based fuels because of their best combustion profile and environment-friendly nature. Despite some challenges, biofuels can provide a useful way to reduce the dependency on non-renewable fossil fuels and can prove beneficial to the environment around us. Biofuels can be produced by various sources like lignocellulosic wastes, plants, algae, starch, vegetable oils, etc. Algae are third-generation biofuels and they have novel properties and important advantages like they can be grown on the land and water, which may be unsuitable for the growth of plants, and they produce biofuel by utilizing the natural resources such as sunlight, water, CO_2, etc. Further, the fourth-generation biofuels, i.e., genetically modified microalgae, have shown potential as an alternative source for biofuel production. Out of the different biofuel production technologies, transesterification is the most convenient process for preparation of biodiesel from oil and fat because they are eco-friendly and carried out under mild conditions.

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