Chapter 1
Biofuel Production Technologies, Comparing the Biofuels and Fossil Fuels

Zahra Shahi and Mohammad Khajeh Mehrizi

Abstracts Current worldwide energy supplies are dominated by fossil fuels (coal, crude oil, petroleum gas). Utilization of oil inferred energy and characteristic concern has elevated to investigate the biofuel as alternate energy bases. Biofuels are the promising option in contrast to modest, ecologically dangerous fossil fuels. Biofuels are alluded to the energy-enriched compounds made over the biological procedures or got from the biomass of living beings, for example, microalgae and vegetation. Biofuels can contribute to reducing greenhouse gas releases, atmospheric pollution, and unnatural weather change. Biofuels classify into two groups: essential and auxiliary biofuels. The essential biofuels are in a flash made from consuming woody or cellulosic matter and dry creature decrement. Auxiliary biofuels may order into three generations. The first generation is biodiesel prepared from waste animal fats, and the next is biodiesel received from oil-rich herbal seed. The last-generation biofuel is produced from microalgae, cyanobacteria, and other microbes.

Keywords Biofuels · Fossil fuels · Biodiesel · Biomass · Plant · Energy

1.1 Introduction

Urbanization, the explosion of population and quick industrialization, has prompted expanded vitality demand. The progress has been phenomenal in the utilization of non-renewable energy sources, comprising coal (29%), natural gas (24%), and oil (35%) (Taparia et al. 2016; Atadashi et al. 2012). According to the International Energy Agency estimation, worldwide vitality request is relied upon to increment by 53% since 2030 (Ashraful et al. 2014).

Nowadays, fossil fuels adopt 80% of the chief energy expended in the universe, where 58% are absorbed through the conveyance section (Singh and Nigam 2014).

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Table 1.1 Outcome of fossil fuel radiations on human safety (Mofijur et al. 2016)

Exhaust emissions	Effects
Formaldehyde	Risk of cancer, eye and nose irritation, nausea
Ozone	Impaired lung function, asthma, headaches
Lead	Hyperactivity and pulled down learning span in children
Carbon monoxides (CO)	Affect fetal progress in anticipant women and tissue growth of young children
Nitrogen oxides (NO_x)	Bronchitis, pneumonia, asthma

Fossil fuels are widely used because of their high heating authority, accessibility, and modality ignition features (Hassan and Abul Kalam 2013).

These fossil fuels have many adverse effects including energy security concerns; increasing oil prices; climate change and global warming; emissions of greenhouse gases such as CO_2, CO, and SO_2; environmental pollution; damage of biodiversity; and others, which conduct to transports and focus to renewable, maintainable, effective, and impressive power sources (Taparia et al. 2016; Atadashi et al. 2012; Singh and Nigam 2014). Table 1.1 displays the result of fossil fuel releases on human safety (Mofijur et al. 2016).

With growing concerns about fossil fuels, biofuels as an environment-friendly energy source have received a large amount of recent attention.

Biofuels are stated as gas, liquid, and solid fuels mainly created from biomass. In other words, biofuels are energy-enriched chemicals made of the biological methods from the biomass of living organisms, for instance, algae, bacteria, and plants (Rodionova et al. 2016). A diversity of energies are created from biomass, for example, ethanol, methanol, biodiesel, etc. (Nigam and Singh 2011).

The biofuel industry is developing, as the consumption of biofuels in the European Union increased by 8% from 2016 to 2017 (Achinas et al. 2019). Asia's biggest biofuel manufacturers are Indonesia, Malaysia, the Philippines, Thailand, China, and India (Jayed et al. 2011).

Biofuel can function as an expansion to the conventional device energies or essential energy in motors. For instance, the strategy for blending the fuel in with ethanol delivered from sugar biomass is generally utilized in Brazil (Voloshin et al. 2016). This chapter is an endeavor to review the biofuel construction organization.

1.2 Classification of Biofuels

Biofuels are categorized into two types: essential and auxiliary biofuels. The essential biofuels are the usual biofuels straightly created from vegetables, wood chips, animal discarded, etc. (Fig. 1.1) (Atadashi et al. 2012; Rodionova et al. 2016). Essential fuels are straightforwardly combusted for the most part to gracefully cooking fuel, warming, or power creation needs in little and huge scope mechanical

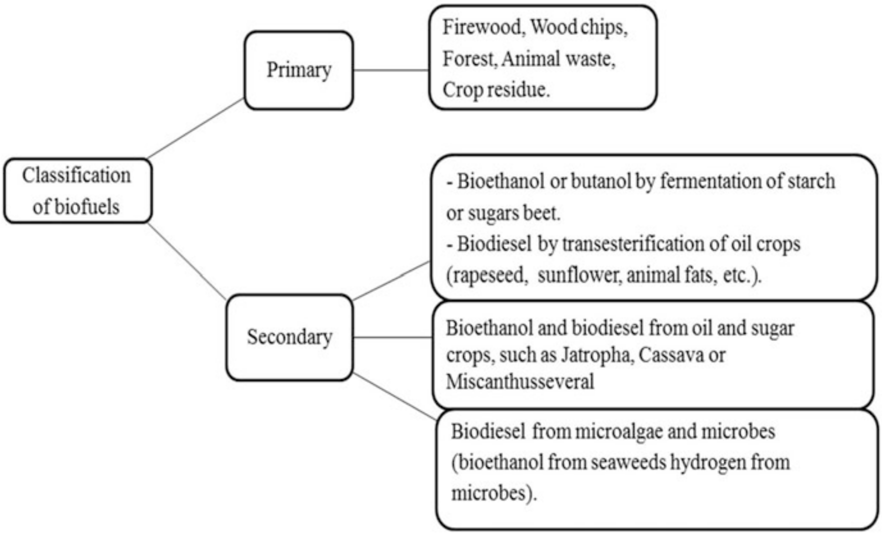

Fig. 1.1 Classification of biofuels (Atadashi et al. 2012; Rodionova et al. 2016)

applications. Auxiliary biofuels have been delivered as solids (charcoal), liquids (ethanol, biodiesel), and gases (hydrogen) (Nigam and Singh 2011).

The biofuels are discrete into three descendants. The first descendant of biofuels is ethanol from starch or sugars and biodiesel from oil crops such as rapeseed, soybeans, and animal fats (yellow grease). The second descendant of biofuels is the creation of bioethanol and biodiesel from numerous kinds of vegetables, for example, jatropha, cassava, karanja, mahua, and camelina. The last descendant is the construction of biodiesel from microalgae and microbes. These comprise algal biomass that utilize as the feedstock for the manufacture of biodiesel (Atadashi et al. 2012; Rodionova et al. 2016). Secondary fuels can be used for numerous usages, containing transport and high-temperature industrial operations (Nigam and Singh 2011).

Biofuels based on plants are being known as a pure and renewable fuel alternative to fossil fuels. The use of these biofuels has advantages contrasted with non-renewable energy sources. These comprise (1) decreased dependency on oil imports, (2) a decline in emissions of greenhouse gas and toxic particular, and (3) economic development in rural areas (Patan et al. 2018).

A diversity of fuels may be manufactured from biomass, for example, biodiesel, bioethanol, biomethanol, biohydrogen, and biomethane (Singh and Nigam 2014). Biodiesel and bioethanol are the two greatest favorable applicants for biofuels (Taparia et al. 2016).

1.3 Biofuel Production: Biodiesel and Bioalcohol

Biodiesel (Greek, bio, life, and diesel from Rudolf Diesel) as a managed energy are resulting from a natural source (Jayed et al. 2011). Biodiesel, as a sustainable power source, can possibly be utilized as a substitute fuel in diesel machines (Atadashi et al. 2012).

Biodiesel is a fuel containing monoalkyl esters of long-chain unsaturated fats that are resultant from renewable biological sources, for example, herbal oils or animal fats (Singh and Nigam 2014). To put it simply, biodiesel can be made from any oil/lipid source. The main apparatuses of these sources (oils and fats) are triacylglycerol molecules (Nigam and Singh 2011).

In other words, biodiesel is made by the esterification of free unsaturated fats or the transesterification of triacylglycerols (Veljković et al. 2018).

Triglycerides are comprised of a glycerin backbone with fatty acid radicals jointed in place of the hydroxyls (Fig. 1.2) (Wen and Johnson 2009; Canakci and Gerpen 2001).

Fatty acids and fatty acid methyl esters with four and more double bonds are vulnerable to oxidation through storing, and this decreases their suitability for consumption in biodiesel (Chisti 2007).

Numerous vegetable oils such as peanut, corn, safflower, soybean, palm, etc. have been utilized to create biodiesel. In the year 1900, the diesel engine by Dr. Rudolf Diesel was run by peanut oil at the Paris Exposition. Biodiesel is formed from non-edible oils like mahua, neem, karanja, and jatropha (Hassan and Abul Kalam 2013). Biodiesel fuel proffers several superiorities compared to petro-diesel fuel. These benefits are:

1. It is sustainable, available, and renewable.
2. It can give modest and nearly fuel for rustic economies.
3. Production has little toxic waste.
4. Biodiesel has greater oxygen quantity than fuel diesel, and its consumption in diesel machines has displayed a noteworthy decline in the radiation of carbon monoxide, sulfur, and polyaromatic hydrocarbons. The use of biodiesel provides a clean environment and can decrease 90% of air poisonousness and 95% of cancers.
5. Producing biodiesel is easier than diesel.

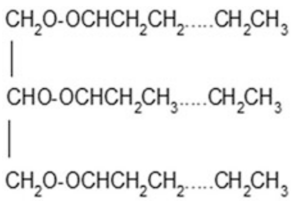

Fig. 1.2 The molecular structure of triacylglycerols (Wen and Johnson 2009)

6. Biodiesel has a high combustion efficiency.

   Combustion is an essential chemical method that discharges energy from a fuel and air mixture. Biofuels, except biohydrogen, are oxygenated combinations. The oxygenated construction could raise the effectiveness of changing the burning energy to power. Lastly, biofuels consume all the more absolutely, hence increasing ignition efficacy. Biodiesel provides a 7% average increase in burning performance.
7. Biodiesel dose not need to be drilled, transported, or refined similar diesel.
8. Biodiesel has an upper cetane number (around 50) than diesel energy. The cetane number is a regularly utilized index for the purpose of diesel energy superiority.

Biodiesel has a destructive nature against copper and brass and causes excessive engine wear (Atadashi et al. 2012; Hassan and Abul Kalam 2013; Xu et al. 2006; Bhatti et al. 2008; Balat and Balat 2010; Demirbas 2009).

Bioalcohol has been utilized as a source of fuel for numerous periods (Rodionova et al. 2016). Alcohol-based fuels have been relevant energy sources since the 1800s. As early as 1894, France and Germany were consuming ethanol in interior combustion engines (Labeckas et al. 2014).

Today, bioalcohol is deliberated as a non-fossil another transport (Rodionova et al. 2016). Ethanol, if it is manufactured utilizing inexhaustible biomass, is termed as bioethanol (Nigam and Singh 2011). Bioethanol is the greatest popular bioalcohol, whereas biopropanol and biobutanol are the less popular.

Bioethanol is known as the flex fuel (Srivastava et al. 2020). There are some sources for bioethanol fabrication, for example, agricultural wastes, maize, potatoes, sugarcane, etc. (Rodionova et al. 2016).

Fermentation of banana (*Musa acuminata*) pseudo-stem to bioethanol is a noteworthy another technology for the creation of biofuels by cellulolytic fungi and yeast (Ingale et al. 2014).

Bioethanol increases energy combustion in vehicles, and it reduced the radiation of carbon monoxide, unburned hydrocarbons, and cancer-causing agents. Blending ethanol in with petroleum helps to lessen the sulfur substance and in this manner brings down the radiations of sulfur oxide. Bioethanol as a fuel is created from sugarcane and accounts for 40% of energy requests for cars, lorries, and buses in Brazil (Nigam and Singh 2011). There are 187 marketable bioethanol plants in the USA that mostly create bioethanol from corn grain (Khan et al. 2018).

Harvests for bioethanol development have been contended because of improved yield cost. In this way, bioethanol creation has been done from different sources, for example, ocean growth (Sukwong et al. 2018).

Algae are an additional basis of bioethanol construction.The general microbe Saccharomyces cerevisiae is an organism used for the effective creation of ethanol through the route of fermentation. Biomethanol can be created by **fermenting or distilling** the crops encompassing sugars and starch. Spirulina sp. is the fastest microalgae that can provide biomethanol (Rodionova et al. 2016).

1.4 Current Feedstock for Biofuel Production

Generally, biofuel feedstock can be characterized into four groups.

1.4.1 Animal Fats

Fats and tallow from animals are the first cluster of feedstock for biofuel construction (Wen and Johnson 2009). Animal fats such as chicken that removed from chicken wastes fat are a low-cost feedstock for biofuel construction (Alptekin et al. 2014).

Contrasted with plant crops, these fats proposed a commercial benefit since they are valued satisfactorily for alteration into biodiesel.

However, animal fat comprises great values of saturated fat that biofuels prepared from this feedstock tend to gel and restrict request for winter-time use (Wen and Johnson 2009). Also, there are significant concerns about biosafety when fats from polluted animals are used (Atadashi et al. 2012).

1.4.2 Oils Derived from Various Crops and Plants

The second group is pure oils derived from soybean, canola, corn, flax, sunflower, etc. (Wen and Johnson 2009). Currently, there are more than 350 probable herbal oil harvests depending upon the weather and soil environments that utilized as the leading conservative feedstocks for biofuel construction (Ghazali et al. 2015).

Most biofuels utilized in the world are prepared from soybean oil and rapeseed oil by transesterification with alcohol (Ingenito et al. 2016). Rapeseed oil is the chief biodiesel originating in Europe, while soybean oil is the greatest public origin for biodiesel fabrication in Brazil, Argentina, and the USA (Mahmudula et al. 2017).

Also, olive pomace oil is a feedstock with hopeful potential for biodiesel production in the island of Crete, Greece (Tsoutsos et al. 2011).

The point that jatropha oil cannot be utilized for dietary purposes without detoxification makes its usage as vitality or biofuel source exceptionally appealing. Jatropha oil was used as an inorganic diesel substitute throughout the Second World War (Akbar et al. 2009).

These oils are pure, and it makes a more quality. However, it can cause an increase in commodity prices and worldwide food (Taparia et al. 2016; Wen and Johnson 2009).

Lengthy utilization of crude herbal oils in diesel machines may expand carbon deposits on the fuel injectors attributable to their limited ignition. This might lead to a failing of device efficiency and cause mechanical harm (Atadashi et al. 2012).

Euphorbia holds high ability as a feedstock source for biofuel progress. Euphorbiaceae-derived fuels have desirable properties. Among these are positive physical attributes, for example, viscosity, density, great vitality content, and satisfactory radiation features (Patan et al. 2018).

1.4.3 Cooking Oils, Meat, and Leather Industry Wastes

The third group of feedstock is discarded cooking oils gathered from schools, cafeterias, restaurants, and households (Atadashi et al. 2012; UTLU 2007).

Free fat acid rates of less than 15% in restaurant waste oils are identified as yellow grease. If the free fatty acid rate overdoes 15%, it is sold as brown grease.

Yellow and brown grease are noteworthy feedstock for the making of biofuels and are cheap compared with vegetable oil (Canakci and Gerpen 2001).

Nevertheless, they comprise major volumes of free fatty acid that fats cannot transform to biodiesel since these react with an alkaline catalyst and **soaps** will made. **Soaps** stop the partition of the wash water, ester, and glycerin (Alptekin et al. 2012).

In other words, the detergents encourage the creation of steady emulsions that stop partition of the biofuels from the glycerin through processing (Canakci and Gerpen 2001).

Reused oils have various polluting influences that require preprocessing to guarantee a biofuel result of stable quality. Preprocessing creates the creation method more complex and expensive (Wen and Johnson 2009). Also, the fat value of the leather industry wastes is incredible. In other words, one method to improve the leather wastes is by consuming them in biofuel manufacture because of their rich fat worth.

Therefore, the contamination produced by the leather business wastes may be condensed (solid waste output from the tannery manner is expected at above 6 million tons/year (Dagne et al. 2019)). The contamination instigated by the meat business squanders ascends with creating yearly meat utilization. The contamination might be diminished, and progressively critical items can be acquired by altering them to biofuels (Alptekin et al. 2012, 2014).

1.4.4 Microorganisms

Several microbial types, for example, yeasts and microalgae, can be utilized as expected wellsprings of biomass for the creation of biofuels (Singh and Nigam 2014). Microalgae are photosynthetic germs that may ascend by CO_2 and sun-oriented light as carbon and vitality bases, separately. They can accumulate components which may be used in numerous businesses, for example, biofuels, effluent treatment, etc. (Fig. 1.3) (Khan et al. 2018; Oh et al. 2018).

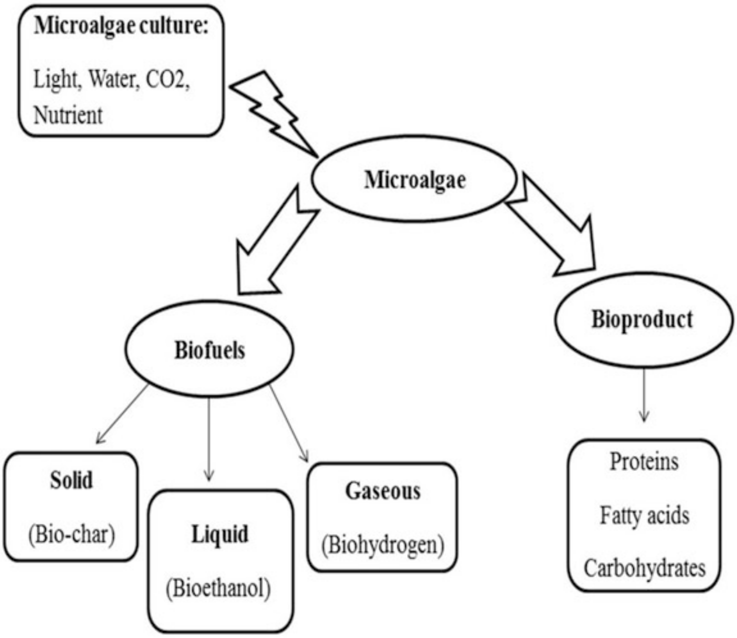

Fig. 1.3 Schematic of microalgae as a source for biofuels and bioactive compounds (Khan et al. 2018)

The microbial lipids, alike to plant oils, comprise palmitic, stearic, oleic, and linoleic acid with unsaturated fatty acids adding up to 64% of the whole fat acid substance (Singh and Nigam 2014).

Microbial oils, as single cell oils for the production of biofuels produced by microorganisms, are believed to be a promising potential feedstock (Zhu et al. 2008). The oil value of algae concerning their dry weight made them the perfect sustainable fuel (Table 1.2) (Adeniyi et al. 2018; Kirrolia et al. 2013).

The oil value of microalgae is generally among 20–50%, whereas certain strains can attain as great as 80% (Table 1.3) (Singh and Nigam 2014; Wen and Johnson 2009; Adeniyi et al. 2018).

Algae oil can be manufactured at speeds of up to 500 times the speed per acre of any other source of plant oil (Taparia et al. 2016). As to similarity of these microorganisms with culture various conditions autonomy from the periods of the year, the fast development rate, engrossing carbon dioxide and improving air quality, sustainability, non-contending with food supplies, microalgae are known as one of the most appropriate alternatives for the biofuel creation (Boshagh et al. 2019).

Contingent upon kinds and cultivation technique, microalgae may deliver biohydrogen, biomethanol, and bioethanol. A few types of green algae, for example, *Botryococcus braunii* and *Chlorella protothecoides*, enclose elevated ranks of terpenoid hydrocarbons and glyceryl lipids. These algae have excessive possibility for the creation of oil fuels likely bioethanol, triterpenic hydrocarbons, and

Table 1.2 Diverse bases for the oil creation and their evaluation (Kirrolia et al. 2013)

Sources of oils	Benefits	Weaknesses
Microalgae	– Fatty acid compositions alike to plant oils – It may have 85% of the dry weight	– The price of cultivation is greater in contrast to crop oils – The greatest algal lipids have lower energy content than diesel energy
Yeasts	– Resources are plentiful in nature – Short period development cycle	– The price of cultivation is greater in contrast to crop oils – Route of oils extracted is complex
Bacteria	– Fast development rate	– Most of bacteria couldn't produce lipids but complex lipoid
Waste	– It is low-priced in relation to crop oils	– Enclosing an excessive saturated fatty acid that is difficult to change over to biodiesel by catalyst

Table 1.3 The oil value of microorganisms (Singh and Nigam 2014; Wen and Johnson 2009)

Germ		Oil value (% dry weight)
Microalgae	*Botryococcus braunii*	25–75
	Schizochytrium sp.	50–77
Bacteria	*Bacillus alcalophilus*	18–24
	Arthrobacter sp.	<40
Yeasts	*Rhodotorula glutinis*	72
	Cryptococcus albidus	65
Fungi	*Humicola lanuginosa*	75
	Mortierella isabellina	86

isobutanol (Rodionova et al. 2016). Figure 1.4 display the factors that ought to be thought of while choosing an algal species for biofuel creation (Taparia et al. 2016).

The biomass from algae, similar to wood, may be burned to create heat and electricity (Wen and Johnson 2009). Heterotrophic growing of *C. protothecoides*, provided with acetate, glucose, or additional biological combinations, results in an extraordinary value of lipid in cells (crude lipid value around to 55.2%). Therefore, *C. protothecoides* has been suggested as an excellent candidate for biofuel production (Xu et al. 2006).

Microbial organisms, for example, *Escherichia coli* and *Saccharomyces cerevisiae* (baker's yeast), are discovered broadly for their probability to create biofuels (Koppolu and Vasigala 2016).

Besides, numerous bacteria kinds such as *Escherichia coli* and *Bacillus subtilis* manufactured upper quantities of bioalcohol (Patan et al. 2018).

The creation cost of algal oil relies upon variables, for example, yield of biomass from the way of life framework oil content, creation frameworks, and the expense of recuperating oil from algal biomass (Ghazali et al. 2015). The employment of microalgal biomass for the creation of biofuels is as of now being viewed as an

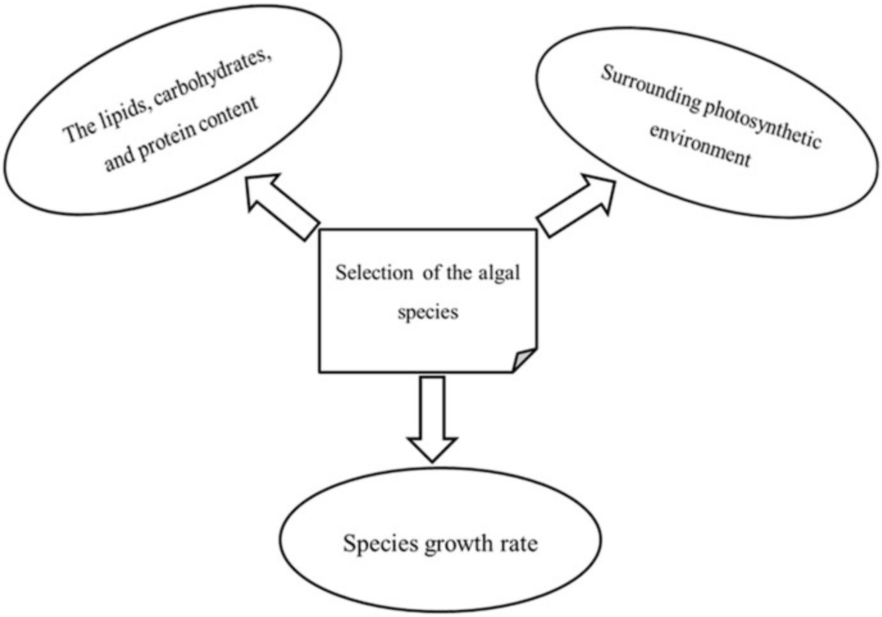

Fig. 1.4 Factors affecting the selection of algae species in biofuel production (Taparia et al. 2016)

Table 1.4 The physicochemical properties and standard specification for biodiesel (Hassan and Abul Kalam 2013)

Properties (units)	USA ASTM D6751	EU E 14214
Flash point (°C)	130	120
Viscosity at 40 °C (cSt)	1.9–6	3.5–5
Cetane number (min)	47	51
Cloud point (°C)	–	–
Oxidation stability (h)	3	6
Acid number	0.5 max	0.50
Phosphorus (% mass)	Max. 0.001	Max. 0.001

appealing alternative for the not so distant future because of helpful effects from the innovation (Klein et al. 2018).

1.5 Classification of Biodiesel

Quality norms for delivering, showcasing, and putting away of biofuel are being created and actualized to keep up the end-product quality. An assessment of biodiesel norms was presented in Table 1.4. The EU and US standards were outlined below (Hassan and Abul Kalam 2013; Gouveia et al. 2017; Ciftci and Temelli 2014).

1.5.1 Flash Point

Flash point is the bottom temperature at which energy yields sufficient vapor to cause blast prompting fire creation. Biodiesel has an upper flash point than arbitrary diesel. Thus, it is a crucial protection standard for transportation and storing.

1.5.2 Viscosity

Kinematic viscosity is a physical property identified with the chain length and degree of saturation. The viscosity of biodiesel is greater than fossil diesel; also, biodiesel develops viscous or even hardened at low temperatures.

1.5.3 Cetane Number

The cetane number denotes the ignition feature of biodiesel in the engine. Normally, biodiesel has a somewhat upper cetane number than fossil diesel. A low cetane number results in a decline in combustion performance and greater gas release of hydrocarbons. The cetane number can increase while raise length of fat acid chain and ester groups.

1.5.4 Cloud Point

Cloud point denotes to the bottom temperature in which crystal construction in biodiesel may be detected. The behavior of fuel at low temperatures is a chief quality norm.

1.5.5 Oxidation Stability

Biodiesel fuels (especially with an extraordinary value of higher unsaturated esters) are extra vulnerable to oxidative corruption than fossil diesel energy because the methylene groups are vulnerable to radical attacks adjacent to the double bonds.

1.5.6 Acid Number

The acid number is a degree of free fatty acids restricted in a new energy example. It is stated in mg KOH necessary to neutralizing 1 g of fatty acid methyl esters.

1.5.7 Phosphorus

Phosphorus in fatty acid methyl esters from phospholipids (animal and vegetable material) and mineral salts (used frying oil) are enclosed in the feedstock.

1.6 Biodiesel Processing Technology

Pyrolysis, microemulsification, transesterification, and direct oil use/blends with diesel fuel, as diverse approaches of making biodiesel from diverse feedstocks, have been advanced. The utmost public process is the transesterification reaction of herbal oils with short-chain alcohols (Atadashi et al. 2012).

1.6.1 Biodiesel Production Via Transesterification

The most common way by transesterification is a catalyzed chemical reaction including alcohol and vegetable oil to produce glycerol and alkyl esters (biodiesel) (Bhatti et al. 2008). The immiscibility of oils with alcohol causes the low alteration of triglycerides to biodiesel production. Consequently, to enrich the reaction degrees, catalysts are employed (Atadashi et al. 2012).

Transesterification reactions include three kinds: acid-catalyzed, alkali-catalyzed, and enzyme-catalyzed. Catalysts are utilized to raise the reaction degree and produce esters. Figure 1.5 is a schematic of the transesterification reaction of herbal oil in the existence of catalyst (Atadashi et al. 2012; Bhatti et al. 2008).

At first, in the catalytic transesterification process, the catalyst is dissolved into the methanol with vital moving in a small reactor. Next, the oil will be moved to the catalyst/alcohol mixture in the biodiesel reactor. The final blend is agitated for 2 h at 340 K in ambient pressure. A fruitful transesterification reaction will create ester and crude glycerin as two liquid phases. The rough glycerin, the heavier of two fluids, will gather at the base following a few hours of settling (Hassan and Abul Kalam 2013).

Homogeneous catalysts include alkaline catalysts (hydroxide, sodium methoxide, potassium hydroxide) and acid catalysts (sulfuric acid, sulfonic acid, hydrochloric acid) (Atadashi et al. 2012).

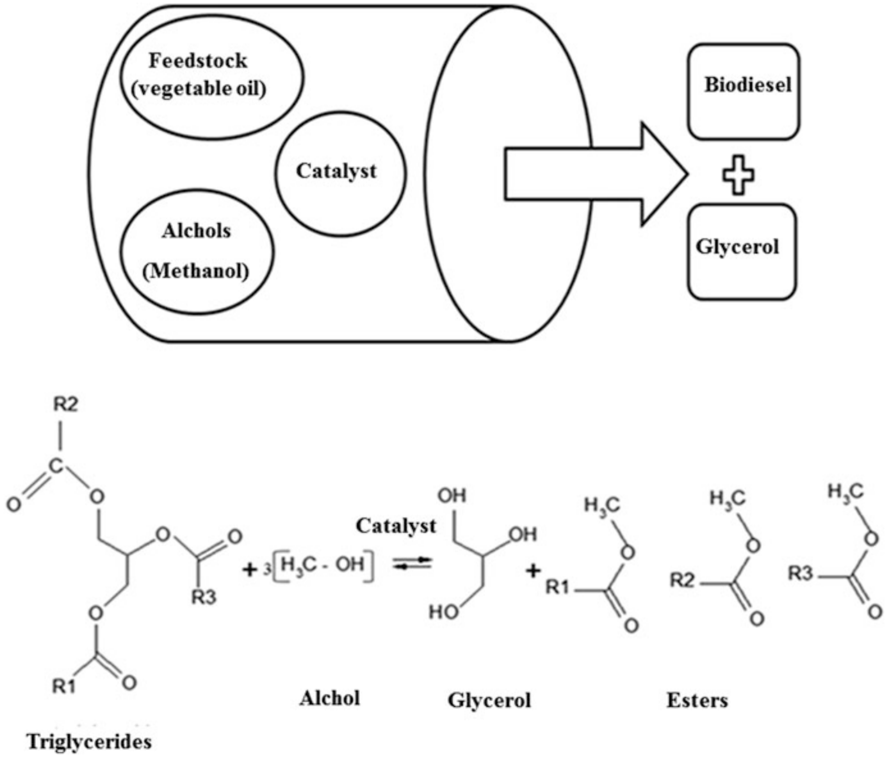

Fig. 1.5 Transesterification of triglycerides (Atadashi et al. 2012; Hassan and Abul Kalam 2013)

Acid catalysts have a lower reaction rate than alkali catalysts. Acid catalysts' transesterification is 4000 times lesser than the alkali-catalyzed reaction (Huang et al. 2010). Enzyme catalyst is more costly than a base catalyst. Hence, base catalysts are favored in the industrial procedure (Fan et al. 2010).

Various types of catalysts utilized for transesterification are enzymes, anion exchange resins, alkaline earth metal combinations, and titanium silicates.

Diverse forms of transesterification methods are exposed in Fig. 1.6 (Hassan and Abul Kalam 2013).

The free fatty acid matters cause noteworthy results on the transesterification of glycerides with alcohol by means of a catalyst (Johanes Berchmans and Hirata 2008).

As stated earlier, the existence of great free fatty acids in the feedstocks renders its processing difficult, because the reaction of saponification by alkaline catalysts leads to soap formation (Fig. 1.7) (Atadashi et al. 2012).

The detergents encourage the creation of steady emulsions that avoid separation of the biodiesel from the glycerin through processing and reduced biodiesel yields

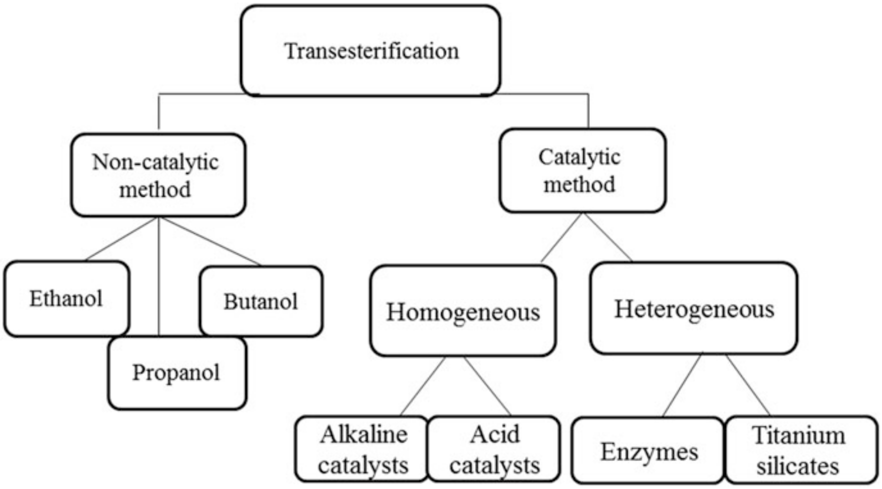

Fig. 1.6 Different types of transesterification (Hassan and Abul Kalam 2013; Jayed et al. 2011)

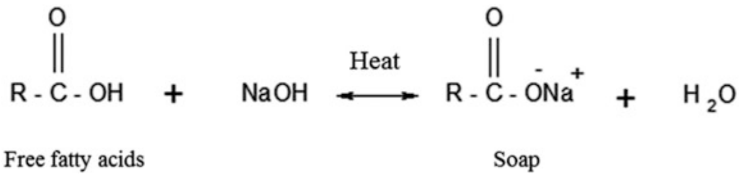

Fig. 1.7 Saponification from free fatty acids (Atadashi et al. 2012)

Fig. 1.8 Creation directions of transesterification and hydro-treated Scheme (Li et al. 2013)

and formation of gels. Still, its viscosity increased (Atadashi et al. 2012; Canakci and Gerpen 2001).

Free fatty acids are transformed to esters over the pretreatment, and thereby, the free fatty acids' level reduces (Alptekin et al. 2012).

Unique in relation to transesterification, hydro-rewarding of herbal oil or animal fat has been created through a few organizations (Neste Oil, Axens IFP). In the hydro-treating procedure, plant oil or animal fat is the feedstock. Hydrogen is added into the herbal to eliminate and saturate the C=C, and the ultimate yields are propane. Propane is likewise a favorable and important energy (Fig. 1.8) (Li et al. 2013).

1.6.2 Transesterification by Supercritical Methanol

Supercritical methanol transesterification is a procedure where the feedstock reacts with supercritical methanol and fats are transformed to biodiesel with extremely condensed time without the usage of a catalyst. Washing and neutralization, owing to the lack of catalyst, aren't wanted.

With this technique, the issue related with this procedure is the prerequisite of great pressure and temperature. The contrast of the change proficiency of diverse feedstock with distinct approaches was displayed in Table 1.5 (Shahid and Jamal 2011).

Several factors such as the molar ratio of alcohol to plant oil, free fatty acid quantity, types of catalysts used, amount of catalyst, temperature, reaction time, and water content have an important effect on the manufacture speed and the quality of the biofuels (Hassan and Abul Kalam 2013; Bojan et al. 2011).

1.7 Algae Biofuel Production

Cultivation, harvesting, drying, cell disruption, lipid extraction, transesterification, hydrolysis, and fermentation are the diverse and complex stages in biofuel production from microalgae.

Cultivation of microalgae is achieved in either an indoor or an outdoor system. Microalgal culture desires to be ventilated with CO_2 and replaced with a growth medium involving nitrogen, phosphorus, and iron (Halim et al. 2012). The lipid extraction method contains mechanical and chemical extractions (Fig. 1.9) (Mubarak et al. 2015).

The chemical manner uses biological solvents such as n-hexane and chloroform, which are poisonous and disturb health and the environment. The supercritical extraction skill reduces the usage of poisonous solvents and uses non-toxic CO_2 gas as a solvent. Ultrasonication and microwave-assisted methods can remove the supreme amount of algae lipids (Mubarak et al. 2015).

Table 1.5 Assessment of yields of methyl esters with distinct approaches (Shahid and Jamal 2011)

Raw material	FFA content wt %	Yields of methyl esters wt%		
		Alkaline catalyzed	Acid catalyzed	Supercritical methanol
Palm oil	5.3	94.4	97.8	98.9
Rapeseed oil	2.0	97	98.4	98.5
Used frying oil	5.6	94.1	97.8	96.9
Discarded palm oil	>20.0	No reaction	No reaction	95.8

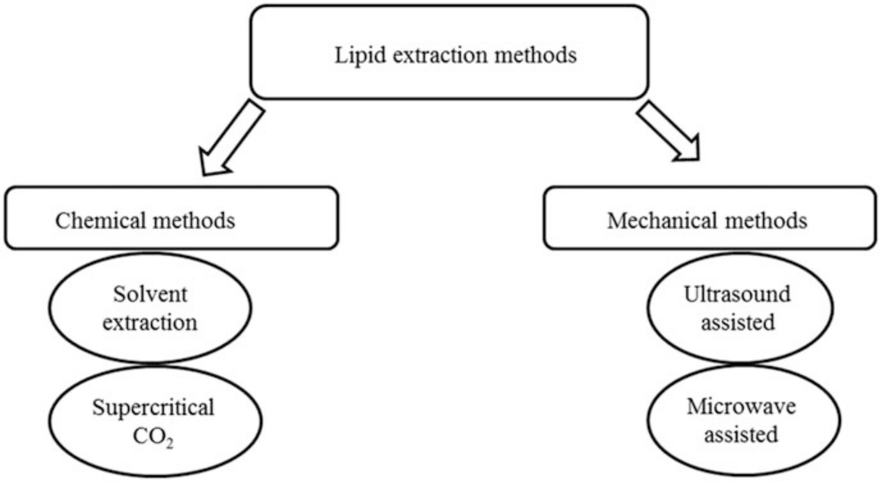

Fig. 1.9 Lipid extraction methods from microalgae (Mubarak et al. 2015)

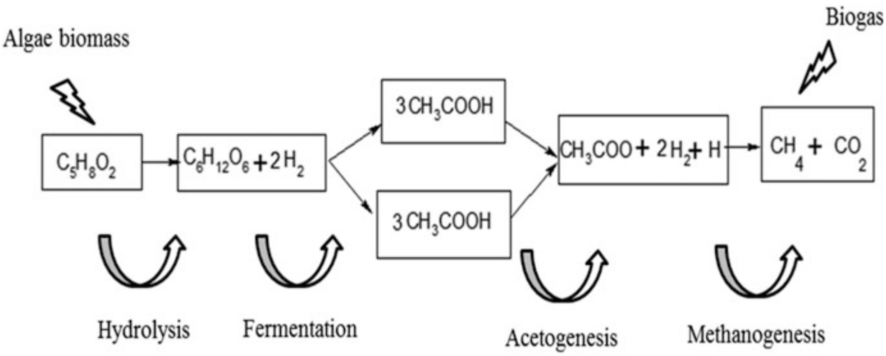

Fig. 1.10 Anaerobic digestion conversion process (Rodionova et al. 2016)

Anaerobic fermentation creates biogas under the lack of oxygen. Anaerobic state helps in the development of germ on natural biomass and exchanges it into methane (60–70%) and carbon dioxide (Srivastava et al. 2020).

In the anaerobic digestion conversion process, the first stage (Fig. 1.10) is hydrolysis whereby algae cell walls should be destroyed down by the bacteria's activities. This is the separating of particulate natural material of algae to soluble sugars and amino acid.

The next stage is the fermentation. Change of soluble sugars and amino acid from the chief step to ammonia, hydrogen, and carbon dioxide occurred in the fermentation stage.

The third step is acetogenesis or the oxidation of fermented products to oxidize all the acids from the fermentation method.

The last stage is methanogenesis or the alteration of hydrogen, carbon dioxide, and ammonia into methane and carbon dioxide (Rodionova et al. 2016).

Production of molecular hydrogen is one of the most hopeful styles in the assembly of sustainable energy. Biohydrogen utilize power fuel cells for power. Photosynthetic organisms, for example, photosynthetic bacteria, cyanobacteria, and green algae, as are skilled in the hydrogen production.

There are two key procedures to the creation of biohydrogen. In the first method (indirect way) is used as the potential of photosynthesis. In some cyanobacteria and green algae, direct water biophotolysis is followed in two stages:

$$H_2O + 2Fd_{ox} \rightarrow 2H^+ + \frac{1}{2}O_2 + 2Fd_{red} \tag{1.1}$$

$$2H^+ + 2Fd_{red} \leftrightarrow H_2 + 2Fd_{ox} \tag{1.2}$$

The first reaction happens in all oxygenic phototrophs, and then the next reaction needs microaerobic or anaerobic situations. The H2 construction reaction is applied by the bidirectional hydrogenase enzyme.

1.8 Research Records on Biofuel Production

Rezaei et al. used grape kernel oil for the making of biofuels by potassium hydroxide and sodium hydroxide as catalysts and methanol. The extreme effectiveness of biodiesel production for KOH (99%) and NaOH (95%) was obtained in ideal situations, for example, methanol-to-oil ratio of 9:1, temperature of 70 °C, 1 wt. % catalyst, and 90 min. Table 1.6 shows several of the physicochemical attributes of the biodiesel (Rezaei et al. 2017).

Alptekin et al. created methyl ester using fleshing oil attained from leather industry fleshing wastes. The results showed the viscosity of the fleshing oil methyl ester decreases with the increasing catalyst amount and methanol molar ratio and catalyst quantity and (Fig. 1.11).

The viscosity impacts the quality of combustion. High viscosity may result in incomplete combustion and increase the engine deposits, while low viscosity may result in leakage in the fuel system.

Table 1.6 The physicochemical properties of biodiesel (Rezaei et al. 2017)

Properties (units)	Biodiesel	USA ASTM D6751
Flash point (°C)	160	<130
Viscosity at 40 °C (cSt)	3.3	1.9–6
Cetane number (min)	52	47
Cloud point (°C)	–	–
Acid content (mg KOH/g)	0.20	0.5 max

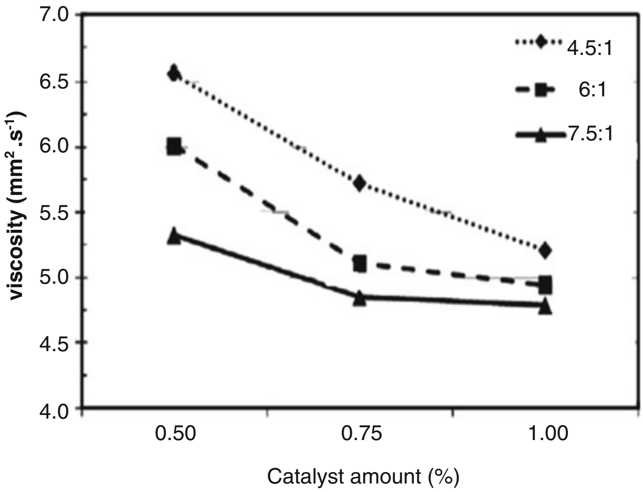

Fig. 1.11 The alteration in the viscosity with the diverse extent of KOH and methanol (Alptekin et al. 2012)

Ester yield is one of the supreme critical factors, which move the biodiesel price (Alptekin et al. 2012). It is considered by dividing the ester extent to the pretreated fat quantity utilized for transesterification (Dagne et al. 2019).

$$\text{Yield } (\%) = \frac{\text{Total weight of fatty acid methyl ester}}{\text{Total weight of oil in the sample}} \times 100 \ (\%) \qquad (1.3)$$

Higher ester incomes, up to 93.6%, were achieved at KOH-catalyzed reactions (Fig. 1.12) (Alptekin et al. 2012).

Bhatti et al. applied chicken fat (98.29% fatty acids) and mutton tallow waste (97.25% fatty acids) for biofuel production. In optimum situations, chicken and mutton fat methyl esters development after 24 h in acid was obtained 99.01% and 93.21%, respectively.

Figure 1.13 indicates the consequence of temperature on the production of biodiesel. The maximum production of biodiesel was gained at 50° and 60 °C for chicken fat and mutton tallow, respectively.

Temperatures higher than 60 °C were not utilized for biodiesel making since at high temperatures, catalyst (H_2SO_4) might hurt oil and entail low produce of biodiesel.

The production of biodiesel was dependent on the catalyst quantity. By increasing the extent of H_2SO_4 from 1 to 3 g, the biodiesel yield of the chicken fat and mutton tallow was improved (Fig. 1.14).

Both fats are very appropriate to create biodiesel with suggested fuel attributes (Bhatti et al. 2008).

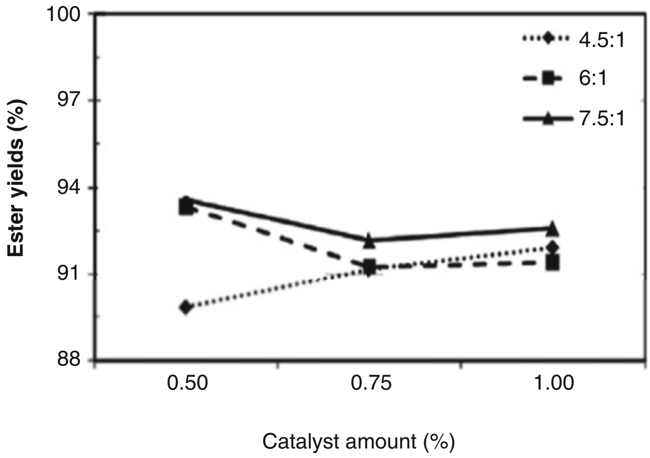

Fig. 1.12 The change in the ester yield with the different amount of KOH and methanol (Alptekin et al. 2012)

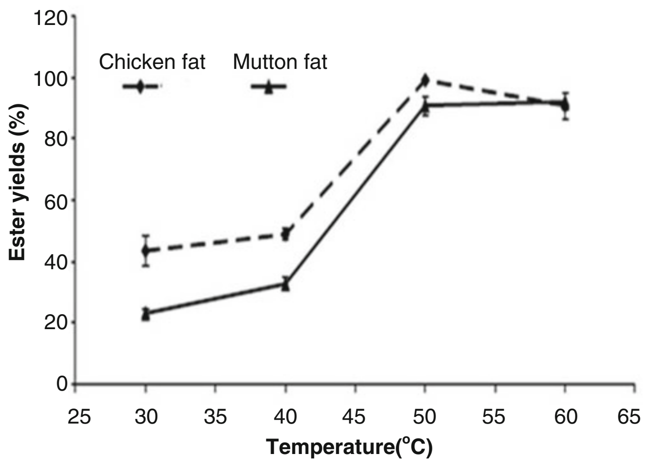

Fig. 1.13 Influence of temperature on the production of biodiesel at 1.25 g catalyst (Bhatti et al. 2008)

Nasaruddin et al. examined the construction of biodiesel from sludge palm oil (51.64% fatty acids) and cheap waste oil through enzymatic catalysis (*Candida cylindracea* lipase).

The result indicated that the chief production of biodiesel (62.3% w/w) was attained at an optimal reaction time of 24 h.

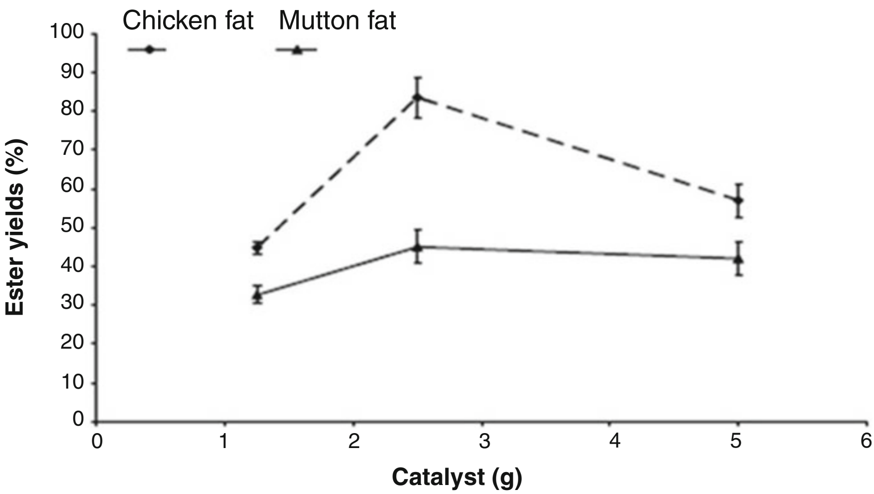

Fig. 1.14 The influence of a catalyst on the yield of biodiesel created (Bhatti et al. 2008)

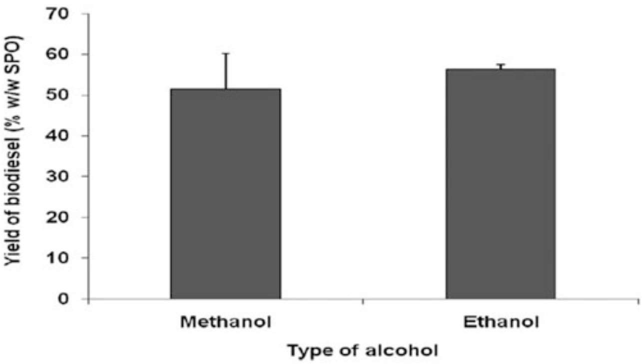

Fig. 1.15 The influence of various alcohols on biodiesel creation (Nasaruddin et al. 2013)

Usually, the reaction time for the chemical biodiesel making is shorter than the biodiesel creation via an enzymatic catalyst.

The results displayed that ethanol provided a greater production of biodiesel in contrast to methanol (Fig. 1.15).

Although, the difference between the yield of ethanol and methanol was small, but in terms of cost and economic benefit and advantages such as higher cetane number, lower cloud points, ethanol can be more attractive as compared to methanol.

Since ethanol would now be able to be delivered from sustainable and ease farming biomass, along these lines, ethanol biodiesel shows up as a 100% inexhaustible other option (Nasaruddin et al. 2013, 2015).

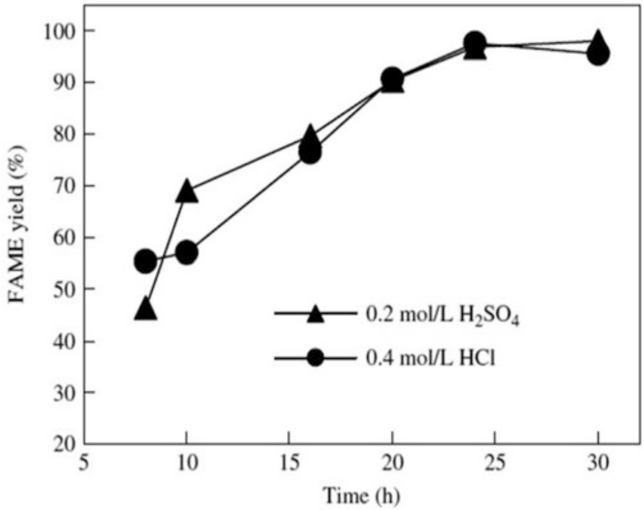

Fig. 1.16 The influence of time on the production of biodiesel with a biomass-to-methanol ratio of 1:20 (w/v) at 70 °C (Liu and Zhao 2007)

Table 1.7 Transesterification of oleaginous strains (Liu and Zhao 2007)

Strain	Lipid content (%)	Fatty acid methyl ester yield (%)	Cetane number
L. Starkeyi	50.2	96.8	59.9
M. isabellina	53.2	91.0	5.4
R. toruloides	58.0	98.1	63.5

Liu et al. produced oleaginous microbial biomass by consuming two yeast strains, i.e., *Lipomyces starkeyi* and *Rhodosporidium toruloides*, and *Mortierella isabellina* as one fungal strain.

The results in Fig. 1.16 exhibit that fatty acid methyl ester (FAME) construction improved over time and more than 90% yield could be attained at nearly 24 h.

Table 1.7 displays a number of the features of the biodiesel in the transesterification of oleaginous strains (Liu and Zhao 2007).

Alptekin et al. utilized corn oil, chicken fat, and fleshing oil to produce biodiesel. The creation price of corn oil methyl ester was greater than those of animal fat because of the significant expense of biodiesel feedstock. Also, the fuel attributes of formed methyl esters were nearby to each other. Notably, the sulfur quantity of the corn oil methyl ester was lower (6.3 ppm) than those of chicken fat (135 ppm) and fleshing oil (>990) methyl esters (Alptekin et al. 2014).

Mirabdoli et al. for biofuel production utilized rapeseed oil. The outcomes exhibited that the best situations for making biodiesel (yield of methyl ester: 78.65%) are methanol-to-oil ratio of 1:6, NaOH content of 0.31%wt/wt, the temperature of 45 °C, and reaction time of 60 min. Table 1.8 shows some of the

Table 1.8 The physicochemical attributes of biodiesel (Mirabdoli et al. 2016)

Properties (units)	Biodiesel	Diesel	Standards
Flash point (°C)	>180	52	ASTM D93
Viscosity at 40 °C (cSt)	4.738	2.7	ASTM D445
Heat value (MJ/kg)	39.18	45.343	ASTM D24
Density at 40 °C	0.882	0.847	ASTM D7042
Sulfur (% mass)	0.882	0.847	ASTM D7042

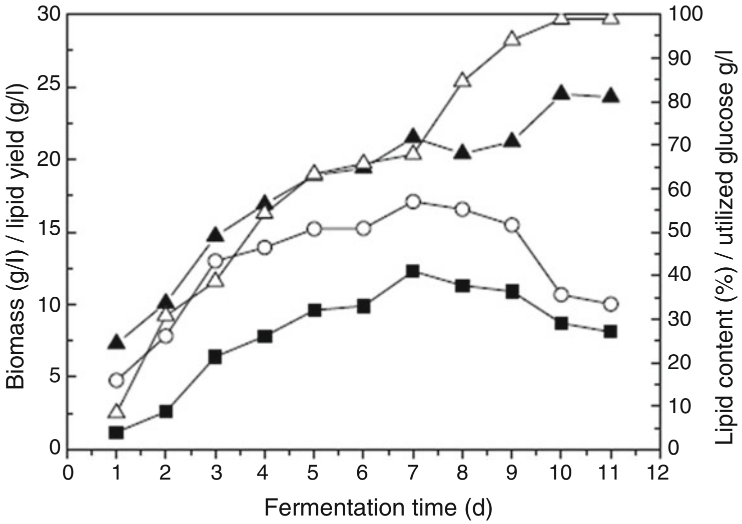

Fig. 1.17 The time course of cell growth and lipid accumulation. (▲) Biomass; (■) lipid yield; (○) lipid content; and (●) utilized glucose (Bhatti et al. 2008)

physicochemical attributes of the biodiesel. As indicated by the outcomes, biofuel is an appropriate substitute for petro-diesel fuel (Mirabdoli et al. 2016).

Zhu et al. studied the creation of microbial biofuel from microbial oil (*Trichosporon fermentans*). The mentioned microbe is a type of yeast and might produce a great quantity of extracellular lipase from olive oil. Like herbal oils, the lipid mostly comprises palmitic acid, oleic acid, linoleic acid, and stearic acid. Figure 1.17 indicated the time course of cell growth, glucose (carbon source) exhaustion, and lipid manufacture of *Trichosporon fermentans*. Biomass, lipid value, and employed glucose slowly improved after the time of inoculation.

The microbial oil with a lipid content of 62.4% (after culture for 7 days, pH, 6.0, T, 25 °C) was transesterified to biofuel and a great methyl ester production of 92% achieved. This yeast can be utilized for delivering modest microbial oil from agro-mechanical deposits for monitoring the natural contamination and biodiesel creation (Zhu et al. 2008).

Rashid et al. studied the oil separated from *Citrus reticulata* seeds as a feedstock for the creation of biofuel. *C. reticulata* comprise 67.4% unsaturated fatty acids,

Table 1.9 The physicochemical properties of biodiesel (Rashid et al. 2013)

Properties (units)	Biofuel	USA ASTM D6751
Flash point (°C)	164	<130
Viscosity at 40 °C (cSt)	4.17	1.9–6
Cetane number (min)	57.6	47
Sulfur content (%)	0.019	0.05 max
Acid content (mg KOH/g)	0.34	0.5 max
Oxidative stability (h)	2.69	3 min
Magnesium	0.01	5 ppm max combined
Phosphorus	1.2	0.001% mass max

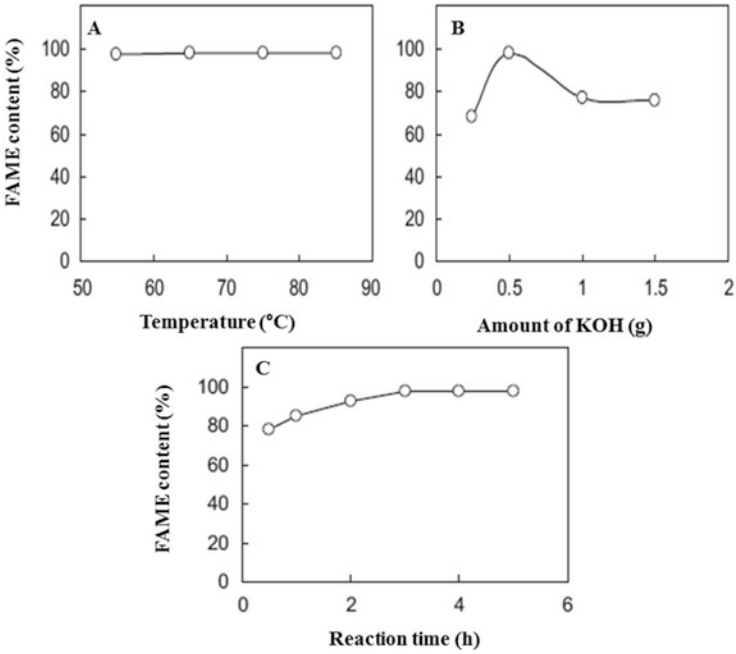

Fig. 1.18 Influence of time, temperature, and content of FAME on the yield of biodiesel (Chung et al. 2009)

while the amount of saturated fatty acid was 32%. Table 1.9 shows some of the physicochemical properties of the biofuel. Generally, biofuel formed from the mentioned seed and likely other citrus seed oils have good potential to the supply of biofuel (Rashid et al. 2013).

Gosavi et al. produced bioethanol by using fruit wastes like Indian water chestnut, sweet potato, jackfruit, and pineapple. An extreme amount of bioethanol was obtained from pineapple waste (0.090% or 0.90 mg/ml) and then sweet potato waste (0.079% or 0.79 mg/ml). The method used was a simple, reliable process

Table 1.10 Investigation of different attributes of manufactured biodiesel (Bojan et al. 2011)

Properties (units)	Raw *Jatropha curcas* oil	Jatropha methyl ester	ASTM standard
Viscosity at 40 °C (mm^2/s)	40.28	4.2	1.9–6.0
Acid content (mg KOH/g)	13.7	0.14	0.50 maximum
Flash point (°C)	220	105	130
Cetane number (min)	51	52.3	47
Sulfur value (%)	0.02% w/w	Nil	15 ppm maximum

for economical bioconversion of the given fruit waste to alcohol. Fruit waste is readily available and helped to decrease the price of biofuel (Gosavi et al. 2017).

Chung et al. employed duck tallow as a feedstock for the making of biodiesel by transesterification with methanol. The consequences disclosed that the high value of fatty acid methyl ester (97%) was achieved at the catalyst amount KOH 1 wt%, reaction temperature 65 °C, and 3 h reaction time (Fig. 1.18) (Chung et al. 2009).

Bojan et al. studied response surface methodology to decide the ideal response situations for the creation of biodiesel from *Jatropha curcas* oil. The consequences revealed that the ideal situations for extreme yield of biodiesel (81.936%) were catalyst amount of 2.06 (% w/w), oil-to-methanol ratio of 1:7.28, reaction temperature of 61 °C, and 90 min reaction time.

Table 1.10 offers the diverse attributes of raw *Jatropha curcas* oil and manufactured biodiesel (Bojan et al. 2011).

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