



Biodiesel from Biomass: Production of Sustainable Biodiesel Fuel

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10.1 Introduction

Biomass availability sources have emerged as a potential alternative to ever-shrinking fossil fuel reserves. In present times, from the overall global energy demand, approximately 81% of the energy is being obtained from fossil fuels, which will negatively impact the environment and human health (Aderibigbe et al. 2021). According to the oil market report (2021) from the Organization of the Petroleum Exporting Countries, the global oil demand could rise from 90.5 to 96.5 million barrels per day (mb/day) from 2020 to 2021, which could be due to the inevitable industrial and anthropogenic overcome of the globally imposed COVID-19 lockdown courses of action taken in 2020. Likewise, utilization of diesel and gasoline for the first quarter of the year 2021 was around 24.0 and 26.3 mb/day, which can increase further. Also, by the year 2030, it is predicted that the oil consumption around the world will rise to 118 mb/day and could ultimately lead to depletion in the global crude oil reserve by 2060 (OPEC 2021; Bharti et al. 2021). In this sequence, India's utility for automobile fuel is more than 0.5. On average, India's annual consumption is about 450 kg/vehicle. Our dependency on fossil fuel-based energy in powering transportation, agriculture, and accommodation indicates

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P. D. Pathak, S. A. Mandavgane (eds.), *Biorefinery: A Sustainable Approach for the Production of Biomaterials, Biochemicals and Biofuels*, https://doi.org/10.1007/978-981-19-7481-6_10

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an alarming situation and calls for immediate actions to preserve the ever-diminishing fossil fuel and search for a better and more efficient alternative to rendering the need without fail (Mohiddin et al. 2021). Fossil-based fuels produce an ample number of harmful products such as CO, NO_x, CO₂, SO_x, and carbon specifically into the environment (Perera 2018; Kumar et al. 2020). Various global initiatives like the Paris Agreement signed by members (191) of the United Nations Framework Convention on Climate Change (UNFCCC) aim at reducing the global risks of climate change through constant attempts (UN 2015).

Thus, researchers are looking for a non-toxic, high-energy capacity, clean, and green alternative to fossil fuels. Biodiesel, on this note, is the most preferred biofuel to be utilized for its inexhaustibility; innocuous, high lubricating qualities; and cleaner-burning properties (Atabani et al. 2012; Kim et al. 2018; Bharti et al. 2021). Biodiesel is clean, cheap, and environment-friendly and emits fewer hydrocarbons, smoke, and toxic gases. Being produced from local resources, biodiesel is considered renewable. A high amount of excess oxygen allows complete combustion and lower emissions. First-generation raw materials like starch and potato through second-generation non-edible oil cakes, waste oils to third-generation algae, and energy crops can generate high-quality biodiesel through a low-cost, simple transesterification process at moderate reaction conditions. The process involves a reaction between triglyceride and alcohol in the presence of an acid or basic catalyst to produce fatty acid alkyl esters and alcohol (Kanwar Gaur and Goyal 2022; Nagappan et al. 2022). High cetane number, longer ignition delay, low ash value, better engine ignition, and emission performance have motivated researchers to explore different blend ratios of biodiesel in petrol (Gad and Ismail 2021; Suzihaque et al. 2022). Another pathway to produce biodiesel is through thermochemical route. Pyrolysis of biomass in specially designed reactors can produce biochar, syngas, and bio-oil of suitable properties. Feedstock type, reaction conditions, and reactor types can affect the relative proportions of products. To produce commercial-scale biodiesel to replace fossil fuel, interest in biomass, including agricultural waste algae-derived biofuel, has risen considerably (Ghesti et al. 2022).

To promote biofuel as a commercial fuel, policies are designed globally. The major bio-ethanol-producing countries are the United States and Brazil. The United States had created around 1557 petajoules with 38% of global biofuel in 2019 (Kohler 2019). India has also proposed a 20% ethanol blending in petrol and 5% biodiesel in the diesel by 2030 as per its National Policy on Biofuels, 2018 (Devi et al. 2021). American standard ASTM D7467 mentions the biodiesel to commercial diesel from 6% to 20%. Blends with 13% are allowed in Brazil, with the target of increasing to 15% by 2023 (Bukkarapu and Krishnasamy 2022).

The present chapter explores the various types of raw materials to be used for biodiesel production, their merits, and their limitations. Different pathways for converting feedstock to biodiesel generation, yield, and multiple factors affecting the quality of biodiesel produced are discussed here. The chapter also compares the performance of catalytic and non-catalytic transesterification processes. The chapter

offers insight into technical, social, and financial barriers hindering the acceptance of biodiesel and the future scope of biodiesel as a commercial fuel.

10.2 Process for Production of Biodiesel

The waste biomass-derived biodiesel process can involve any of the two routes. The first pathway is the production of lipids through hydrolysis of cellulose and hemicellulose of biomass, which can be further processed to produce biodiesel. The second pathway involves the production of cheap and eco-friendly catalysts from waste biomass components, like stems, leaves, stalks, etc., to enhance the speed of the conventional transesterification process of multiple raw materials (Fig. 10.1).

10.2.1 Enzyme-Catalyzed Biodiesel Production

Biomass consists of lignin, cellulose, and hemicellulose, which are difficult to be converted into simple sugar using conventional methods. Lignocellulosic materials can undergo pretreatment (physical, chemical, or biological) to produce biomass of suitable properties. Pretreatment can involve physical, chemical, or biological methods. Mechanical treatments like milling, grinding, and steaming increase surface area and improve raw material conversion (Wang et al. 2021). Chemical treatment, including acid treatment, enhances cellulose decomposition efficiency. Alkali treatment is done to remove lignin altogether. Biological treatment methods like microbial treatment can be done in a low-cost, environment-friendly manner to degrade hemicellulose and lignin (Mahmood et al. 2019). Cellulase consists of endo-1,4- β -glucanase, cellobiohydrolase, and β -glucosidase, which can be converted into sugar to utilize biodiesel further. Oleaginous microorganisms including yeast, mold, and bacteria, under suitable conditions, can convert carbohydrates into microbial lipids, also known as single-cell oils (SCOs).

Yeast species such as *Meyerozyma guilliermondii* and *Rhodospiridium fluviale* have shown significant lipid production potential. Further, biodiesel can be produced using both catalytic and non-catalytic processes. Non-catalytic processes include treatments like emulsification, pyrolysis, and transesterification, among which transesterification is the most popular.

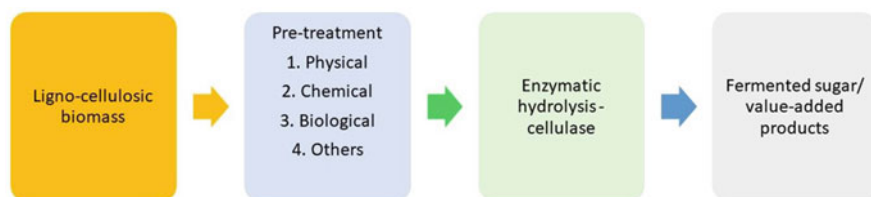


Fig. 10.1 General lignocellulosic biomass utilization process

10.2.2 Transesterification Process

The general procedure for oil extraction involves various common steps. The feedstock is pretreated to enhance oil yield during the pressing stage. Kernel removal and drying are carried out using stompers and mallets, followed by oil extraction. Figure 10.2 shows the general biodiesel production process.

10.2.3 Oil Extraction

Mechanical extraction can be done using a manual ram or an automated screw press. An oil yield as high as 91% on filtering and degumming can be achieved. The solvent extraction process involves using a solvent to extract oil from the seed. The most common solvent, n-hexane, can generate oil of 41% and 95–99% yield using *J. curcas* and *P. pinnata* seeds. There are associated environmental concerns related to wastewater treatment after the solvent extraction process. The enzymatic process uses an enzyme to extract oil from sources. Though the process is slow, it is still an attractive technique due to its eco-friendly nature and no volatile component emission. Recently, researchers have used a combination of solvent extraction and microwave-based hybrid processes to enhance the oil yield efficiency at low cost, time, and energy.

10.2.4 Transesterification

As shown in Fig. 10.2, the oil extracted from the seed is sent for the transesterification process, which is the heart of the biodiesel production process. Since reactants, oils, and alcohols are immiscible with each other, there is a need to mechanically agitate the vessel or increase the reaction time and temperature with additional costs. Reaction temperature, time, mixing intensity, and reactor geometry are the most significant parameters. The production can be done using both catalytic and non-catalytic methods. For the non-catalytic process, the transesterification of vegetable oil takes place above the critical temperature and pressure (temperature, 513 K methanol and 514 K ethanol and 10–45 MPa) (Da Silva and Oliveira 2014). However, high temperatures lead to increased energy consumption and are not economically feasible. The catalytic process utilizes biocatalysts or chemical

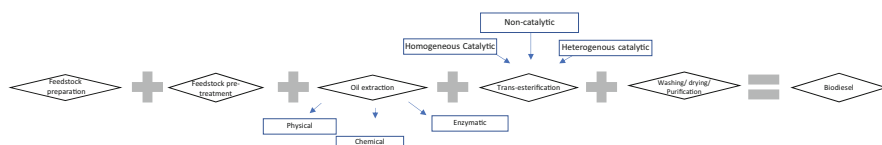


Fig. 10.2 General biodiesel production process

catalysts to transform the triglyceride molecules into fatty acid alkyl esters (FAAEs) (Nasreen et al. 2018; Gupta and Rathod 2021).

Catalytic processes can be further classified into various categories based on the types of material of construction, i.e., homogeneous or heterogeneous types. If a catalyst is soluble in the reactant, it becomes a simple, low-energy-consuming homogeneous catalyst. Certain limitations are associated with a low recovery rate and less reusability (Mohiddin et al. 2021), which prompted researchers to look for heterogeneous catalysts. Being produced from insoluble materials, they are easily detachable using simple centrifugation or filtration processes and are reusable many times. Recently biomass-derived heterogeneous catalysts have gained wide popularity among researchers worldwide (Cheng and Li 2018). Nanocatalysts, including nanoferrites synthesized from ceramic material, showcase tremendous advantages over traditional heterogeneous catalysts regarding their chemical, physical, structural, electrical, and mechanical characteristics (Thakur et al. 2020).

10.2.5 Homogeneous Catalysts

Homogeneous catalysis involves the application of catalysts present in its liquid form, mainly basic and acidic. Homogeneous catalysts such as acids (H_2SO_4 , HCl , H_3PO_4 , $AlCl_3$, $ZnCl_2$, etc.) and bases ($NaOH$, KOH , CH_3NaO , CH_3KO , etc.) are among the widely used catalysts. While homogeneous acid catalysts require high temperature and pressure (Marchetti et al. 2011), homogeneous base catalysts need milder conditions (Vyas et al. 2010). The drawbacks mentioned above notably showcase the inevitable difficulty in separation and reusability of the catalyst and restrict its significance and use in biodiesel's industrial-scale synthesis by using homogeneous catalysts (Bharti et al. 2021).

Homogeneous base catalysts accompanied by milder reaction condition like low temperature and pressure conditions, easy availability, and shorter reaction time (4000 times faster than acid-catalyzed transesterification) make homogenous base catalysts highly acceptable (Kawashima et al. 2009; Williams 2015). Generally, the base catalytic transesterification process undergoes at a minimum pressure (1.4–4.2 bar), temperatures (333–338 K), with a minimum concentration of catalyst (0.5–2 wt%), atmospheric pressure, average stoichiometric alcohol/oil molar ratio, and reaction times (typically 1 h) (Bhuiya et al. 2016).

The mechanism for the action of homogeneous base catalyst is given in Fig. 10.3. Verma et al. (2017) used both methanol and ethanol for the synthesis of Karanja biodiesel through KOH as a catalyst and reported the highest yield of 88.7% and 77% for methanolysis and ethanolysis, respectively, at a reaction temperature of 333 K with a molar ratio of 1:9 and 1.25 wt% of catalyst loading for 2 h. In another study, the waste soybean oil was transesterified with 7 wt% $NaOH$ and gave 95% biodiesel yield with an oil-to-methanol molar ratio of 1:9, reaction temperature of 40 °C, and reaction time of 1 h 33 min (Tan et al. 2019). Another study reported that canola oil is transesterified using $NaOH$ catalyst (3 wt%), yielding 85% biodiesel at

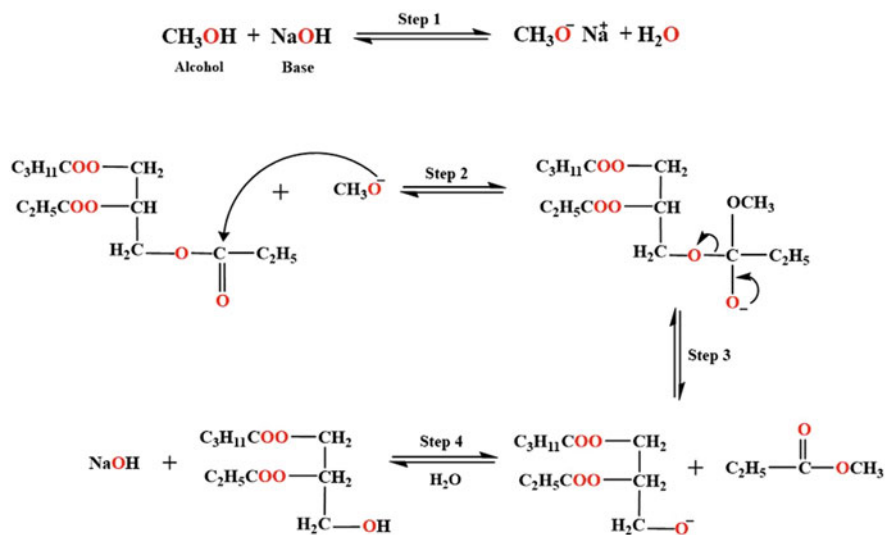


Fig. 10.3 Mechanism for base-catalyzed transesterification process. (Source: Kumar et al. 2021)

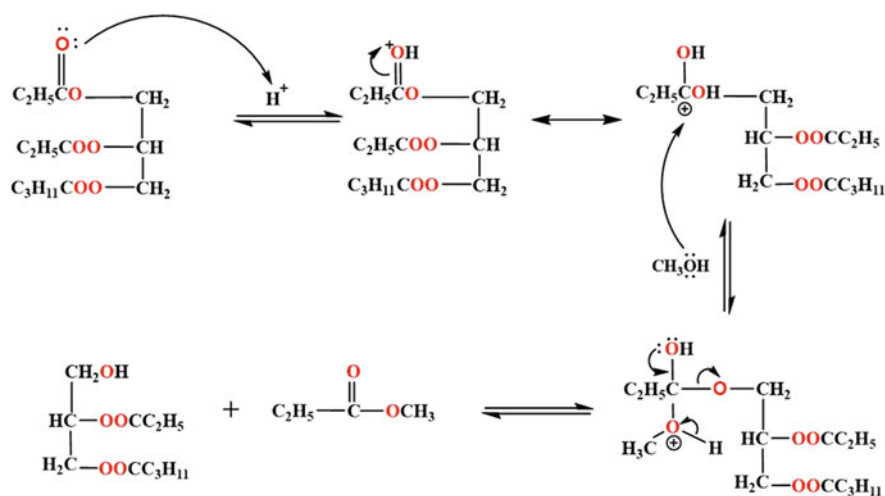


Fig. 10.4 Mechanism for acid-catalyzed transesterification process. (Source: Kumar et al. 2021)

the oil-to-methanol molar ratio of 1:6.5 at a slightly higher temperature of 70 °C for 2 h (Hariprasath et al. 2019).

The most commonly used acid catalysts are sulfuric acid, ferric sulfate, hydrochloric acid, and sulfonic acid (Atadashi et al. 2013). The acid-catalyzed reaction proceeds between triglycerides, alcohols, and an acid catalyst, producing glycerol and biodiesel. Figure 10.4 shows the homogeneous acid-catalyzed reaction mechanism. Unlike base catalysts, acid catalysts are more economically viable and

insensitive to the oil's free fatty acid content. Sulfuric acid and hydrochloric acid are favored catalysts in this process (Lam et al. 2010). Oliveira et al. (2017) reported the yield of biodiesel as 93.5% using H_2SO_4 as a catalyst with oil to methanol ratio of 1:9 at a temperature of 70 °C. The alcohol-to-oil molar ratio is crucial in influencing the reaction.

10.2.6 Heterogeneous Catalysts

Heterogeneous catalysts are anti-corrosive and can be recovered quickly. This ease of recovery attributes to its different reactant phase systems, which assist an easy pathway for separating the catalyst from the reaction mixture through conventional separation techniques like filtration, sedimentation, and centrifugation (Diamantopoulos 2015). Examples of acidic heterogeneous catalysts are ZnO/I_2 , $\text{ZrO}_2/\text{SO}_{2-4}$, $\text{TiO}_2/\text{SO}_{2-4}$, niobic acid, sulfated zirconia, amberlyst-15, and Nafion NR50. In contrast, CaO , CaTiO_3 , CaZrO_3 , CaO-CeO_2 , CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{KOH}/\text{Al}_2\text{O}_3$, KOH/NaY , $\text{Al}_2\text{O}_3/\text{KI}$, ETS-10 zeolite, and alumina/silica-supported K_2CO_3 are some examples of alkali heterogeneous catalysts (Leung et al. 2010).

A suitable heterogeneous catalyst must be mesoporous, highly stable, benign, and inexpensive (Changmai et al. 2020). It must also possess multi-functionality and strong, active sites, making it highly versatile and competitive (Chouhan and Sarma 2011). Presently, researchers are trying to make bifunctional heterogeneous catalysts that can be employed for both esterification and transesterification simultaneously, which could save energy, time, material, and production cost (Farooq et al. 2013; Mohiddin et al. 2021).

The commonly used solid catalysts are functionalized by sulfonated zirconia (SZ), Nafion resins, sulfonated saccharides, tungsten oxides, and organosulfur mesoporous silicas (Chopade et al. 2012). For instance, around 95% yield of biodiesel was obtained from neem oil at a temperature condition of 65 °C for a reaction time of 2 h with a catalyst loading of 1 and molar ratio of 9:1 (alcohol to oil) using sulfated zirconia as a catalyst (Muthu et al. 2010). Another study by Shu et al. (2010) reported the use of carbon-based solid acid catalyst at a temperature of 220 °C with a catalyst loading of 0.2 with the molar ratio of 16.8:1 (alcohol to oil) for 4.5 h using waste vegetable oil as a feedstock for the conversion of biodiesel which yielded to be 94.8%.

The heterogeneous alkali catalyst shows enhanced catalytic activity during transesterification under milder reaction conditions (Calero et al. 2014). Table 10.1 displays several types of base heterogeneous catalysts used for the transesterification of lipids. Researchers have reported the complete conversion (100% conversion) to biodiesel of soybean oil using snail shell as a heterogeneous base catalyst at room temperature with the reaction time of 7 h at the oil-to-methanol molar ratio of 1:6 and a catalyst loading of 3 wt% (Laskar et al. 2018).

Several researchers experimented with kitchen waste as a heterogeneous base catalyst and found encouraging results. Likewise, researchers have obtained a biodiesel yield of 93% by transesterification of refined soybean oil at a temperature

Table 10.1 Effect of catalyst on soybean oil on conversion efficiency

Feedstock	Catalyst	Catalyst (wt%)	Reaction condition (T (°C)/time)	Conversion (%)	MOA: MMEOH	Reference
Soybean oil	Oyster shells	25	65/5	96.5	1:6	Nakatani et al. (2009)
Waste soybean cooking oil	NaOH	0.5	55/2	68.5	1:3	Hossain and Mazen (2010)
Soybean oil	NaOH	1.3	40/1.33	95	1:9	Silva et al. (2011)
Soybean oil	Snail shell	3	RT/7	100	1:6	Laskar et al. (2018)
Refined soybean oil	Chicken eggshell	7	57.5/3	93	1:10	Goli and Sahu (2018)
Soybean oil	MnCO ₃	2	180/1	98.1	1:21	Wan et al. (2018)
Soybean oil	Potassium methoxide	2	80/0.25	91	1:6	Celante et al. (2018)
Soybean oil	MgO supported on γ -Al ₂ O ₃	5	60/6	60	1:6	Navas et al. (2018)
Soybean oil	<i>Brassica nigra</i> waste	7	65/0.42	98.79	1:12	Nath et al. (2019)
Sunflower oil	<i>Sesamum indicum</i> waste	7	65/0.67	98.9	1:12	Nath et al. (2020)
Soybean oil	<i>Moringa</i> leaves	6	65/2	86.7	1:6	Aleman-Ramirez et al. (2021)

of 57.5 °C and reaction time of 3 h with 1:10 to be the molar ratio of oil to methanol at a catalyst loading of 7 wt% (Goli and Sahu 2018). Using chicken eggshell as a heterogeneous catalyst at 57.5 °C for 5 h and the oil-to-methanol ratio of 1:13 with 8.5 wt% of catalyst loading reported 90.41% biodiesel yield (Kirubakaran and Arul Mozhi Selvan 2018).

10.2.7 Nanocatalysts

Along with the development of heterogeneous catalysts, which are recyclable, stable, highly selective, and efficient, demand has been growing simultaneously concerning its improvement or modification as a catalyst that can be used for biodiesel production. Nanocatalysis has emerged as a suitable option. According to the reports, the market value of nanocatalysts had reached up to USD 9.58 billion in 2020, which is further expected to reach USD 22.9 billion by 2027. Nanoscale heterogeneous catalysts with larger surface areas allow them to be an attractive candidate for transesterification reactions (Bharti et al. 2020, 2021). Their catalytic properties can be modified accordingly by simply making acceptable changes to the shape and size of the active phase of the nanomaterials (Somorjai and Materer 1994). Nanoferrites exhibit strong ferrimagnetic properties containing iron oxide as the prime component. They are classified as (a) spinel (MFe_2O_4), (b) garnet ($M_3Fe_5O_{12}$), and (c) hexagonal ($MFe_{12}O_{19}$), where M denotes transition metals like Mn, Fe, Co, Ni, Cu, and Zn (Bharti et al. 2020; Punia et al. 2020; Rana et al. 2015). The introduction of magnetic property into nanocatalyst helps with easier separation. It shows good recovery on applying an external magnetic field which facilitates the minor catalyst weight loss and high catalyst reusability compared to traditional separation techniques (Gardy et al. 2019). Amidst all the base nanocatalysts available to prepare biodiesel, CaO, zeolites, and hydrotalcite have received humongous attention. Among them, CaO has been extensively studied for its high activity, basicity, and milder reaction condition. Despite its advantages, it also shows some limitations in the recovery step of the catalyst from the reaction mixture, as during the process of a transesterification hydrogen bond is formed between the lattice oxygen species with methanol and glycerine, which increases the viscosity of glycerine and forms solid in suspension with CaO which hence inhibit the process of recovery (Kouzu and Haidaka 2012). Magnetic functionalized CaO helps overcome these limitations. Thus, a magnetic material is combined with the CaO and SrO samples to prepare a magnetic catalyst. This prepared catalyst was utilized to transesterify soybean oil into biodiesel by Zhang et al. (2016) and obtained a yield of 94.9% at 70 °C for 2 h with an oil-to-methanol molar ratio of 1:12 and 0.5 wt% of catalyst loading (Bashir et al. 2022). As the magnetic property of the catalyst allowed it to be recovered quickly after every cycle, it showed stability upon five reusable runs.

The biodiesel obtained using the oil extraction process possesses high viscosity and low volatility, contains polyunsaturated hydrocarbons, and is not suitable for use as a fuel. It needs further purification and modification to be used in vehicles (Table 10.2).

Table 10.2 Biodiesel processing technologies

Process	Specific reaction conditions	Advantages	Limitations	Reference
Ultrasonic	<ul style="list-style-type: none"> • Energy = 1.4 kWh/m³ • Biodiesel yield = 99% • Alcohol-to-oil ratio = 4:1 to 15:1 • Frequency = 20–40 kHz • Catalyst = 1–6 wt% • Temperature = 40–65 °C • Time = 15–240 min 	<ul style="list-style-type: none"> • Reduce reaction time and temperature • Low operation cost • Reduce catalyst amount • Increase yield of biodiesel production up to 99% 	<ul style="list-style-type: none"> • Difficult to scale-up • Required specially designed equipment • High installation cost • Energy consumption 	Topare et al. (2015), Bashir et al. (2022)
Microwave	<ul style="list-style-type: none"> • Energy = 500–800 W • Alcohol-to-oil ratio = 3:1 to 18:1 • Catalyst = 0.5–5 wt% • Reaction temperature = 40–100 °C • Reaction time = 0.05–1 h • Conversion yield = 80–100% 	<ul style="list-style-type: none"> • Less time-consuming • Improve biodiesel yield • No pretreatment required • Cleaner products • Less heat loss 	<ul style="list-style-type: none"> • Difficult to scale-up • Need strict control of the time of reaction • Not efficient for materials with high solids 	Bashir et al. (2022), el Sherbiny et al. (2010)
Plasma	<ul style="list-style-type: none"> • Reaction temperature = 25–50 °C • Reaction time = milliseconds–2 min • Conversion yield = 78–100% 	<ul style="list-style-type: none"> • Low reaction time • Less energy required 	<ul style="list-style-type: none"> • Specially designed reactors require • High installation cost 	Kongprawes et al. (2021)
Supercritical	<ul style="list-style-type: none"> • Pressure = 22.5–40 MPa • Temperature = 250–350 °C • Residence time ~ 20 min • Yield = 0–94.04% • Reaction time = 2–120 min 	<ul style="list-style-type: none"> • Less reaction time • Clean and eco-friendly process • No pretreatment required 	<ul style="list-style-type: none"> • High installation as well as running cost 	Quesada and Olivares (2010)

10.3 Scope and Challenges for Biodiesel Usage

The properties of biodiesel are a vital function of the type of feedstock used, with non-edible oils and waste materials as the most promising for its preparation. As a sustainable option, biodiesel is producible in more significant amounts from vegetable oils and fats of animal origin. The choice of raw material for biodiesel production depends on the availability of bio-resources in that specific region. As shown in Table 10.3, based on research trends, it was found that while countries like Cuba, India, Malaysia, Mali, Mozambique, Pakistan, Peru, Tanzania, Thailand, and Zimbabwe have explored *Jatropha curcas*, similarly, oilseed palm was researched in Brazil, Iran, Malaysia, Mexico, Peru, and Thailand; rapeseed in Canada, Chile, China, Greece, Italy, and Turkey; sunflower in Argentina, Canada, Greece, Italy, and Turkey; *Pongamia pinnata* in Australia, Bangladesh, and India; *Callophyllum inophyllum* in Australia and Malaysia; soybean in Argentina, Canada, Italy, and the United States; fish oil in Iran; used cooking oil in Ireland; animal fat and fish residues in Norway and Bangladesh; and microalgae in China as feedstock materials (Alagumalai et al. 2021; Jayakumar et al. 2021). Computing biodiesel from biomass is an acceptable strategy for the future bioenergy-based economic development path.

Other factors like reaction temperature, reaction and holding time, types of catalyst used, and reactor configuration also affect the quality and yield of biodiesel. Different researchers have examined various sources and response conditions to maximize oil output. Optimizing reaction parameters is essential to obtain biodiesel at a low cost. Further experiments are underway to alleviate the properties of biodiesel. Using convention transesterification methods, biodiesel with properties compared to conventional diesel oil can be obtained. As shown in Table 10.4, the flashpoint of biodiesel is 171 °C, much higher than mineral diesel. Thus, they are highly safe to use. In addition to this, the cetane number of biodiesel is much higher

Table 10.3 The majority explored raw materials in different countries (Alagumalai et al. 2021; Jayakumar et al. 2021)

Raw material explored	Countries
<i>Jatropha curcas</i>	Cuba, India, Malaysia, Mali, Mozambique, Pakistan, Peru, Tanzania, Thailand, and Zimbabwe
Oilseed palm	Brazil, Iran, Malaysia, Mexico, Peru, and Thailand
Rapeseed	Canada, Chile, China, Greece, Italy, and Turkey
Sunflower	Argentina, Canada, Greece, Italy, and Turkey
<i>Pongamia pinnata</i>	Australia, Bangladesh, and India
<i>Callophyllum inophyllum</i>	Australia and Malaysia
Soybean	Argentina, Canada, Italy, and United States
Fish oil	Iran
Animal fat and fish residues	Norway and Bangladesh
Microalgae	China

Table 10.4 Pros and cons of using different catalysts

Classification	Pros	Cons	Examples	References
Heterogeneous base catalyst	<ul style="list-style-type: none"> • Upgraded selectivity • Anti-corrosive • Multi-utilizable and reusable • Showcase longer lifetime • Easily separable from product • Faster reaction rate than acid catalyzed 	<ul style="list-style-type: none"> • The high molar ratio of -OH to oil • Fragile to FFA and oil • Diffusion limitation • Hygroscopic • Excess production of wastewater during purification • Poisoning of catalyst when exposed to ambient air • Leaching of functional species 	CaO, CaTiO ₃ , CaZrO ₃ , CaO-CeO ₂ , CaMnO ₃ , Ca ₂ Fe ₂ O ₅ , KOH/Al ₂ O ₃	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Heterogeneous acid catalyst	<ul style="list-style-type: none"> • Simultaneous occurrence of esterification and transesterification • Easy separation b/w product and catalyst • Recyclable, reusable, and regenerative • Suitable for low-grade oils 	<ul style="list-style-type: none"> • Expensive and low rate of reaction • High-temperature conditions and extended reaction time • Unfavored side reactions • Larger energy requirement • Contaminated endpoint due to leaching at the active site 	ZnO/I ₂ , ZrO ₂ /SO ₂ ⁻⁴ , TiO ₂ /SO ₂ ⁻⁴ , niobic acid, sulfated zirconia	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Homogeneous base catalyst	<ul style="list-style-type: none"> • Zero production of water during transesterification • 4000 times faster than acid catalyzed • Moderate reaction conditions and less energy required 	<ul style="list-style-type: none"> • One-time use • Thin-skinned to FFA in oil • Extra step to remove catalyst • Saponification requires the presence of more >2 wt.% of FFA in oil • More waste H₂O is produced 	NaOH, KOH, CH ₃ NaO, CH ₃ KO	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)

(continued)

Table 10.4 (continued)

Classification	Pros	Cons	Examples	References
	<ul style="list-style-type: none"> • Inexpensive, economically feasible, and widely available 	<ul style="list-style-type: none"> • Reduced biodiesel yields due to saponification 		
Homogeneous acid catalyst	<ul style="list-style-type: none"> • High biodiesel yield production • Avoidance of saponification can be achieved • Esterification and transesterification taking place at the same time • Thick-skinned to FFA and water in oil 	<ul style="list-style-type: none"> • Require catalyst neutralization • Corrosive in nature • Lower rate of the reaction • Hard separation of catalyst and product • Additional step for catalyst removal 	H ₂ SO ₄ , HCl, H ₃ PO ₄ , AlCl ₃ , ZnCl ₂	Aderibigbe et al. (2021), Mohiddin et al. (2021), Velusamy et al. (2021), Tamjidi et al. (2021)
Nanocatalyst	<ul style="list-style-type: none"> • Eco-friendly and low toxicity • Easy magnetic separation • Good reactivity, selectivity, and optimum yield • Higher specific surface area • Easy alteration to the physical and chemical properties of the catalyst according to its selectivity and activity 	<ul style="list-style-type: none"> • High in expense • Agglomeration and precipitation • Require high alcohol % • Low rate of reaction • Saponification catalyst deactivation 	Cs/Al/Fe ₃ O ₄ , KF/CaO–Fe ₃ O ₄ , CaO/MgO, KF/Al ₂ O ₃	Velusamy et al. (2021), Tamjidi et al. (2021), Chang et al. (2011), Boz et al. (2009), Feyzi et al. (2013), Hu et al. (2011)

than conventional diesel, indicating its high combustion efficiency (Mishra and Goswami 2018). Researcher investigations have shown that using the ultrasonic method in the traditional process of transesterification can lead to the production of biodiesel with better lower heating values, lower viscosity, and density at less reaction time (4 min) (Ponnappan et al. 2021). Similar experiments are underway globally to improve the properties of biodiesel to improve its utilization potential further. Table 10.4 shows the benefits and drawbacks of various catalysts.

The cetane number of biodiesel indicates its compatibility with engines, including smooth start and running, i.e., engine knock and nitrous oxide emissions (Abomohra

et al. 2022). While high heating value (HHV) defines its calorific value, fuel's viscosity and blending ratio of biodiesel to diesel are the fundamental properties affecting the engine's performance. Table 10.5 shows the properties of biodiesel, including its kinematic viscosity, cloud point, and cetane number obtained from different sources, which are in the range mentioned by the American Society for Testing and Materials (ASTM) and European Standards.

Non-edible oils like palm oil and cottonseed oil are attractive options to prepare biodiesel of international standards. In addition to this, locally available and low-cost biomass feedstocks are also investigated as a potential source of biodiesel. However, the significant challenges with biodiesel are its high viscosity, leading to the formation of larger droplets, poor fuel combustion, and deposition of black smoke in the combustion chamber. The polymerization of unsaturated fatty acids at higher temperatures results in gumming and injection choking. Transesterification of oil is the most common method to reduce viscosity and improve engine efficiency. A few investigations have shown concerns like low stability against oxidation, lack of long-duration shelf life, high cetane number, and high flash point compared to fossil fuels. The studies have shown that lowering NO_x emission is still a challenge by using non-edible oils as substitutes in diesel engines.

Thus, biodiesel blending with petroleum fossil fuels has already been implemented worldwide. Various terms are used to define the proportion of biodiesel in petroleum. Bzz indicates the relative balance of biodiesel, where zz is the quantity of biodiesel in the blend. For instance, B20 and B80 terms are used to define 20% and 80% biodiesel.

10.4 Global Biodiesel Policies

In an attempt to foster the growth of biofuel production to improve the share of renewable energy, different countries have initiated various policy-level interventions like mandatory blending targets, tax exemptions, etc. The ethical issues with first-generation edible products have given impetus to research on biofuel production from non-edible oil cakes and waste biomass material. National biofuel policies of Brazil, India, and Indonesia are generally framed by leveraging the use of local resources like sugarcane, agro-waste, and palm oil, respectively (Saravanan et al. 2018; Lima et al. 2020; Halimatussadiah et al. 2021). Studies have shown that shells of groundnut, rubber seed, castor seed, sunflower, linseed, groundnut, and sesame seed can be used to produce biodiesel in Bangladesh annually. In addition, the country is reported to have a great potential to use non-edible waste animal skin to produce biodiesel (Mahmud et al. 2022).

Initially, the European Commission 2003 Biofuel Directive to increase the use of biofuel and other renewable fuels to 5.75% has impacted both production and consumption of biofuel in European nations. While biofuel policies in Brazil were driven by the petroleum fuel shortage, the US policies were framed to reduce greenhouse gas emissions in the framework. The Canadian Environmental Protection Act Bill C-33 (Canada), Renewable Fuel Standard (RFS2) (the United States),

Table 10.5 Properties of biodiesel compared to US and European Standards

Biodiesel type/standard	Kinematic viscosity (mm ² /s)	Cloud point (°C)	Cetane number	HHV (MJ/kg)	Oxidation stability (h)	Reference
ASTM D6751	1.6–6.0	–	>47	–	>3	Zahan and Kano (2018)
EN 14214	3.5–5.0	–	>51	–	>6	Zahan and Kano (2018)
Diesel	2.5–5.7	–10 to –5	45–55	42–45.9 (calorific value)	–	Ashraf et al. (2014)
Mineral diesel	2.956		46	45.34		Pali and Kumar (2016)
Karanja biodiesel	6.56	8	–	35.82 (calorific value)	–	Khan et al. (2018)
Palm oil biodiesel	4.42–4.76	–	59.9–62.8	37.2–39.91	–	Zahan and Kano (2018)
Cotton seed biodiesel	4.0–9.6	–	41.2–59.5	37.5–41.68	–	Zahan and Kano (2018)
<i>Jatropha</i> oil	4.84	2	51–52	39.63	–	el Sherbiny et al. (2010), Singh et al. (2021), Aigba et al. (2021)
Sal seed methyl ester	5.89		63.5	39.65		Pali and Kumar (2016)
Kusum methyl ester	5.19		57.86	41.6		Pali and Kumar (2016)
<i>Sterculia foetida</i> biodiesel obtained by conventional transesterification process	4.1		64	38.13 (lower heating value)		Ponnappan et al. (2021)
<i>Sterculia foetida</i> biodiesel obtained by ultrasonic stirring transesterification process	3.8		67	38.48 (lower heating value)		Ponnappan et al. (2021)
<i>Protosiphon botryoides</i>	6.41	–2.62	51.59	41.51	5.52	Abomohra et al. (2022)
<i>Chlorella pyrenoidosa</i>	0.14	–2.51	51.64	41.50	3.79	Abomohra et al. (2022)
<i>Scenedesmus dimorphus</i>	3.63	–	32.9	40.2	5.6	Abomohra et al. (2022)

National Alcohol Program Protocol (Brazil), EU Directive 2009/28/EC (European Union), National Policy on Biofuels 2018 (India), and National Policy on Biofuels (Malaysia) are some of the critical global policies targeted at supporting research and development activities and commercialization of the same. In Germany, the Biofuel Quota Act, 2007, had set a target of 4.4% biodiesel in diesel, which was supported by many other policy initiatives like targeting a share of 18% for renewables to total energy share (Saravanan et al. 2018).

Key instruments adopted in the United States to promote biofuel production are supporting the feed crop supply, which include incentivizing farmers to grow biomass feedstock through the Biomass Crop Assistance Program (BCAP). Likewise, the Biorefinery Assistance Program assists biorefineries by providing easy loans (Saravanan et al. 2018). Import tariffs also play a significant role in protecting national industries from the external competition (Sorda et al. 2010). Technology, policies, environmental sustainability, and economics are the pillar of success for biofuel implementation programs.

Overall, the success of these policies depends on competition from other fuels and faster implementation of these policies. Issues related to efficient land use, soil health, and biodiversity need to be addressed through multifaceted, efficient policies encompassing these dimensions.

10.5 Conclusion and Future Direction

Biofuels are fuels obtained from biological sources and take much lesser time to form than fossil fuels. It can play a critical role in mitigating climate change, improving global energy security, and strengthening local economies. Four generations of fuels have been tested under lab and industrial-scale conditions. There are ethical issues associated with the first and second generations of raw materials where edible feedstock is used for biodiesel generation. Thus, more focus should be given to the application of third and fourth generations of fuels, which can serve the dual purpose of waste utilization and energy generation. With more advanced technology like synthetic biology-based raw materials, supercritical oil extraction, and ultrasonic treatment, plasma reactors are tested on a laboratory scale to improve the final product yield and quality.

The potential of biodiesel to replace conventional fuel is very high. Already many nations have adopted biodiesel blends with diesel oil. For many years, international and national policy-makers are also making efforts to reduce fossil fuel usage. Their focus is to encourage low-carbon technologies, and develop energy-efficient technologies. The reduction in environmental CO₂ was observed due to biodiesel in the place of fossil fuels. It may be so because the ratio between CO₂ emitted from biodiesel combustion is lesser than the CO₂ utilized by the plants for photosynthesis (Lapuerta et al. 2008). SO₂ emission was also lower using biodiesel (Basha et al. 2009). Newer techniques like particulate traps, catalysts, and recirculation of exhaust gas can also further improve the efficiency of biodiesel-based vehicles. Though sulfate and aromatic compound emissions are very low, research efforts are still

underway to improve engine performance and reduce nitrous oxide emissions from biodiesel-based fuels.

With the collective efforts from researchers across the globe in advanced reactor configuration, along with the use of third and fourth generations of biofuel and optimization of reaction parameters, the scope of biodiesel as a low-cost, eco-friendly, and sustainable fuel is very high.

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