

CHAPTER 4

Transesterification methods

Bheru Lal Salvi

Department of Mechanical Engineering, College of Technology and Engineering, Maharana Pratap University of Agriculture and Technology, Udaipur, Rajasthan, India

4.1 Introduction

Development in the field of renewable energy generation has widely opened research scope for biodiesel production. Biodiesel is derived from renewable feedstock like vegetable oils and animal fats, and it consists of long-chain fatty acid esters. The biodiesel is typically made by chemically reacting lipids such as vegetable oil (e.g., soybean oil), waste cooking oils, pyrolytic/bio-oils, and animal fat (tallow) with alcohol, producing a methyl, ethyl or propyl ester. The conversion of vegetable oils and tallow into biodiesel is called "*Transesterification*." In organic chemistry, transesterification is the process of exchanging the organic group R'' of an ester with the organic group R' of alcohol. Biodiesel is designated as methyl (or ethyl) esters of fatty acids produced during a reaction to split the triglyceride in fatty acids (Feng et al., 2010; Helwani et al., 2009).

The reactions are often catalyzed by the addition of an acid or base catalyst. The reaction for the conversion of bio-oil to biodiesel is known as the esterification or transesterification reaction according to the use of acid or basic catalysts (Dhawane et al., 2018; Salvi & Panwar, 2012). The schematic diagram for biodiesel production from the feedstock oil is shown in Fig. 4.1. The overall process of biodiesel production includes transesterification reaction, recovery of unreacted methanol, purification of methyl esters from the catalyst, and separation of glycerin as a co-product from saponified products (Kusdiana & Saka, 2001; Salvi & Jindal, 2013; Salvi et al., 2013).

After the transesterification reaction, the glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, the glycerol and ester are separated. This separation usually occurs quickly and may be accomplished with either a settling tank or a centrifuge. Water may be added to the reaction mixture after the transesterification is completed to improve the separation of glycerol (ASTM, 2002; Stidham et al., 2000).

Biodiesel is a monoalkyl ester of triacylglycerol, in the chemical reaction known as transesterification in which fatty acid reacts with any alcohol and form monoalkyl ester (biodiesel) in the presence of a catalyst. There are mainly three types of catalysts, namely, acidic, basic, and enzymatic, which are in use for biodiesel production. The basic chemical process that occurs during the reaction of biodiesel production is given

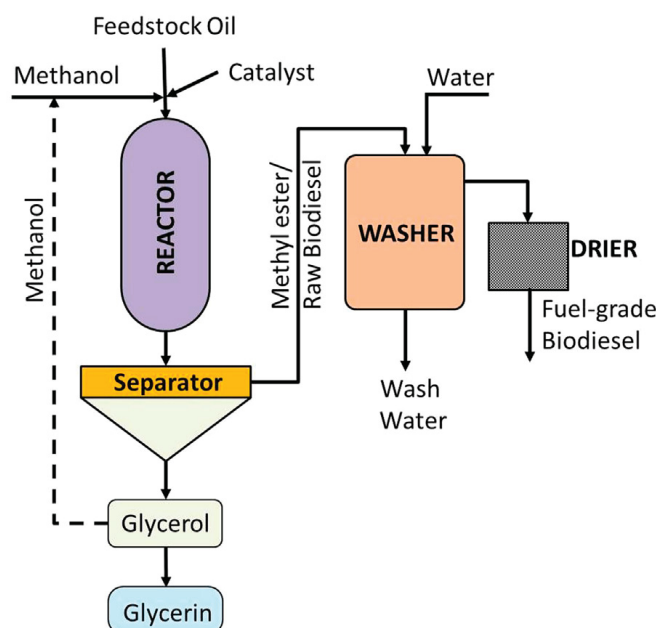


Figure 4.1 Process flow schematic for biodiesel production.

by Eq. (4.1). The triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of a methyl ester of a fatty acid.



The most important issue during biodiesel production is the completeness of the transesterification reaction. The incomplete transesterification reaction results in residues of the triglycerides, diglycerides, and monoglycerides in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as the total glycerol. As per the specification described in ASTM D6584, the total glycerol should be less than 0.24% of the final biodiesel product (Stidham et al., 2000).

There are numerous methods of biodiesel production including chemical methods and biological methods as shown in Fig. 4.2. The chemical methods require ester and catalyst for esterification and transesterification processes, while biological methods require enzymes. The chemical methods are well established and widely being used for biodiesel production. The biological methods are more eco-friendly, but these are being used at the laboratory and research levels. Further research is required to use biological methods of biodiesel production with economic feasibility.

The transesterification reaction generally occurs in three steps, where triglyceride reacts with methanol to produce diglycerides, then diglycerides again react with

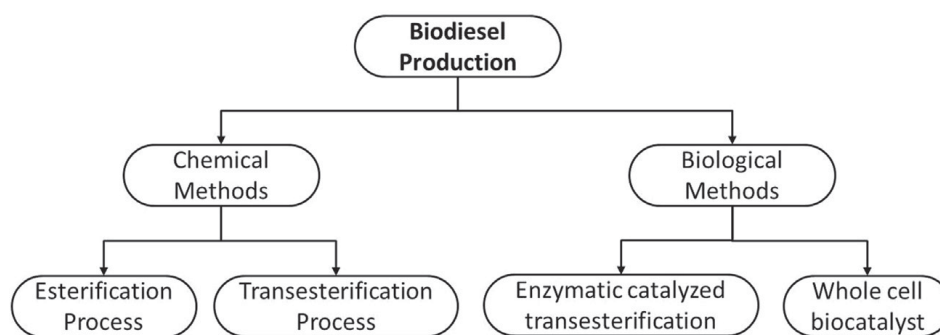


Figure 4.2 Biodiesel production methods.

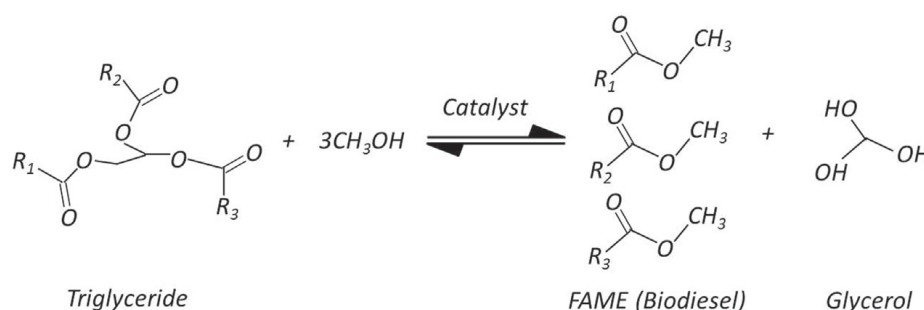


Figure 4.3 Overall transesterification reactions for biodiesel production. From Faruque, M., Razzak, S., & Hossain, M. (2020). Application of heterogeneous catalysts for biodiesel production from microalgal oil—A review. *Catalysts*, 10, 1025. <https://doi.org/10.3390/catal10091025>.

methanol to produce monoglycerides, and finally reacts with an alcohol (i.e., methanol, ethanol) to yield ester (i.e., methyl or ethyl ester) and glycerol (Faruque et al., 2020; Kusdiana & Saka, 2001). The one-step version for the overall transesterification reactions for biodiesel production is given by Eq. (4.2) and Fig. 4.3.



The transesterification process proceeds initially with protonation followed by nucleophilic addition. Further transfer of proton neutralizes the reaction and elimination of R'OH alcohol starts, which is ended with the final product (Faruque et al., 2020). The detailed acid-catalyzed transesterification mechanism is shown in Fig. 4.4.

The duration of the completion of reactions depends on various reaction parameters. The rate of reaction of the above Eq. (4.2) can be calculated by the rate expression as given by Eq. (4.3).

$$\text{Rate} = - \frac{d(\text{TG})}{dt} \quad (4.3)$$

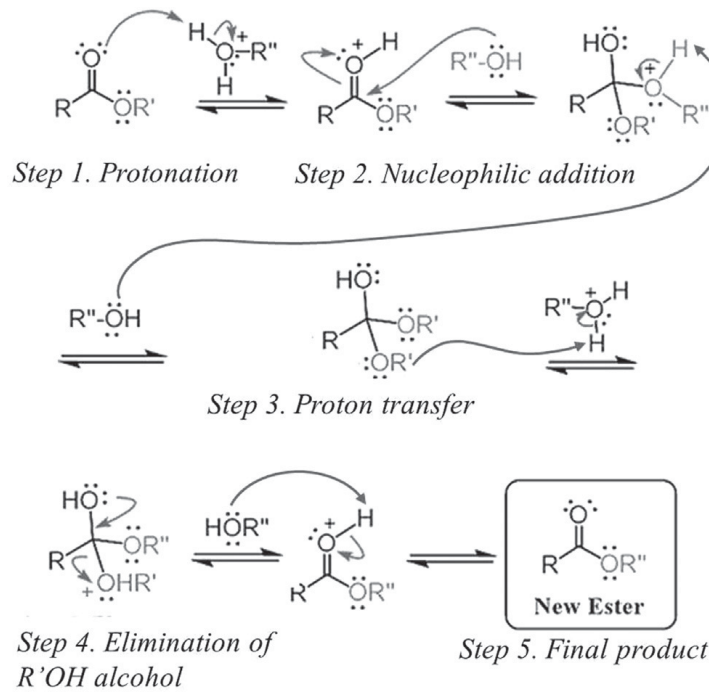


Figure 4.4 Acid-catalyzed transesterification mechanism.

where TG refers to the substance of non-edible oil utilized in that study. In the supercritical alcohol method, three species were well-defined as unalkyl esterified compounds (U_{ae}), alkyl esters, and glycerol. The U_{ae} comprise monoglycerides, diglycerides, triglycerides, and unreacted free fatty acid (FFA). The above rate expression Eq. (4.3) can be modified as Eq. (4.4) (Kusdiana & Saka, 2001).

$$\text{Rate} = - \frac{d(U_{ae})}{dt} \quad (4.4)$$

Commonly, the overall reaction rate is articulated in the Arrhenius equation form, as given by Eq. (4.5).

$$\text{Rate} = - \frac{d(U_{ae})}{dt} = A \times \exp\left(-\frac{E}{RT}\right) \times (u_{ae})^n \times (AL)^m \quad (4.5)$$

where AL refers to alcohol, A is rate constant, and m and n are the constants. The entire reaction is assumed to proceed as First-order reaction (Faruque et al., 2020; Kusdiana & Saka, 2001). The transesterification reaction time and conversion are generally affected by various factors (Ramadhas, 2011), such as oil type and sources of the oil, oil temperature, reaction temperature, ratio of alcohol to oil, type of catalyst and concentration, intensity of mixing, and purity of reactants. Depending upon the

various factors, the yield of biodiesel varies. The percentage yields of biodiesel is calculated on weight basis, as given by Eq. (4.6).

$$\text{Yield}(\%) = \frac{\text{Weight of biodiesel produced}}{\text{Weight of raw oil used}} \times 100\% \quad (4.6)$$

4.2 Chemical method of biodiesel production

Conversion of non-edible and edible oils into biodiesel is done through chemical methods, where esterification and transesterification reactions occur. Esterification is the process of combining an organic acid (RCOOH) with an alcohol (ROH) to form an ester (RCOOR) and water; or a chemical reaction resulting in the formation of at least one ester product. Ester is obtained by an esterification reaction of an alcohol and a carboxylic acid. Transesterification is the conversion process of one type of carboxylic acid ester into a different type of carboxylic acid ester. The transesterification process is a reversible reaction and is carried out by mixing the reactants—fatty acids, alcohol, and catalyst.

The most common method of transesterification is the reaction of the ester with an alcohol in the presence of an acid catalyst. A strong base or a strong acid can be used as a catalyst. The commonly employed alkali catalysts are sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), potassium hydroxide (KOH), and potassium methoxide (CH_3OK). The acid catalysts like sulfuric, phosphoric, hydrochloric, and sulfonic acids are used in such esterification as well as transesterification reactions; however, sulfonic acid is preferred (Thangaraj et al., 2019).

The transesterification reaction requires a suitable catalyst to enable the fate oil into biodiesel with reasonable conversion rates. A wide variety of catalysts can be utilized to produce biodiesel from various raw materials. The classification of various catalysts used for biodiesel production from different raw materials is shown in Fig. 4.5. In the overall transesterification process, the reaction condition and post-treatment hierarchy are preset by the characteristic of the catalyst used. Traditionally, the majority of

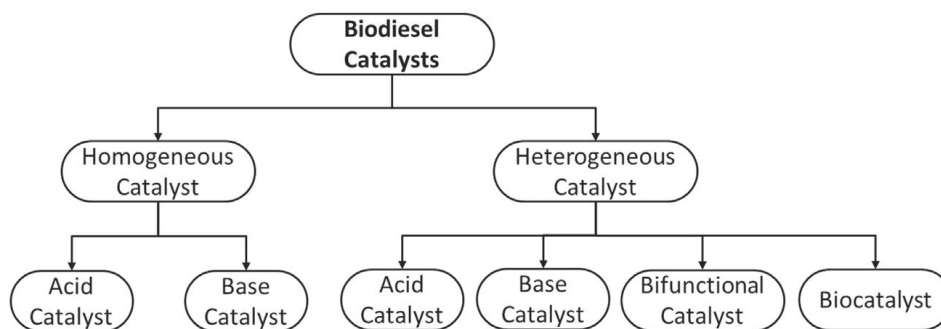


Figure 4.5 Catalysts used for biodiesel production.

biodiesel is produced with alkaline catalysts, such as NaOH and KOH, because of their broad accessibility and low price (Faruque et al., 2020).

4.2.1 Homogeneous catalytic transesterification

The common homogeneous base catalysts used in the transesterification process are NaOH, CH_3ONa , and KOH. All the homogeneous base catalysis processes are done either with NaOH or KOH in the presence of methanol or ethanol (Agarwal et al., 2013; Hoang et al., 2013). A generalized flowchart of the homogeneous transesterification process is given in Fig. 4.6.

4.2.1.1 Acid-catalyzed transesterification

Acid catalysis is the most suitable method in the case of organic substrates. When excess acid is added, better conversion of triglyceride is obtained. Advantages of acid-catalyzed transesterification are direct biodiesel production from low-cost lipid feedstocks, such as waste cooking oil and greases.

Acid-catalyzed transesterification of Karanja oil: The Karanja oil is taken in a biodiesel reactor and preheated up to 100°C using heating media and stirred continuously for 10 min in order to remove any water present with oil. Then heated oil is allowed to cool. When the temperature reaches 65°C , methanol in oil (molar ratio of 6:1) and 1% H_2SO_4 are added (Agarwal et al., 2013). The oil is constantly stirred while

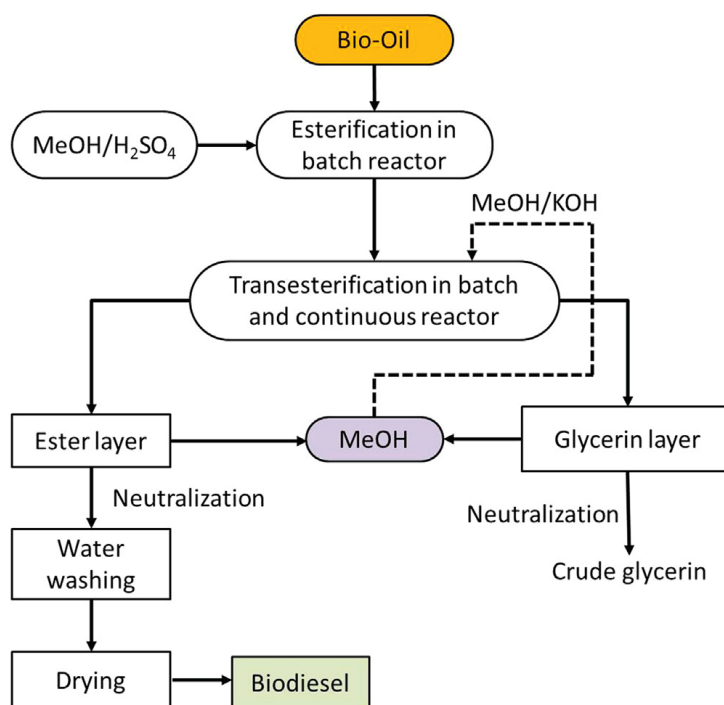


Figure 4.6 Flowchart of homogeneous transesterification process.

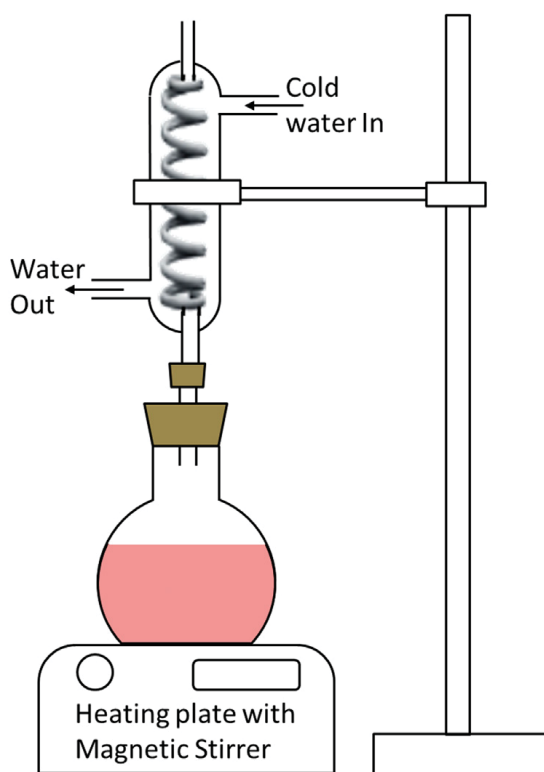
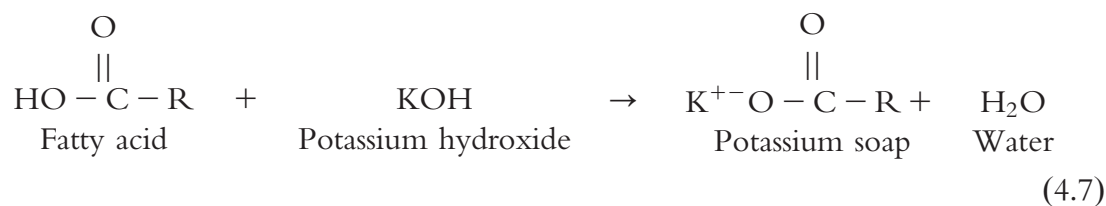


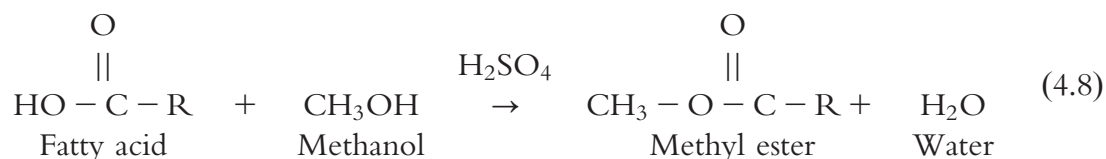
Figure 4.7 Reflux type condenser for bio-diesel reactor.

maintaining the temperature at 65°C. A reflux condenser, as shown in Fig. 4.7, is used so that methanol vapors get condensed and can be trapped back into the reactor. The mixture is allowed to react completely with the alcohol in presence of H_2SO_4 for 2 h. After completion of the reaction, the acid value (0.5–2.0 mg KOH/g oil) of the sample is calculated to check whether it is within the prescribed limit of base-catalyzed transesterification. The sample is then used for base-catalyzed transesterification reaction in both batch and continuous reactors.

Acid-catalyzed pretreatment: Fatty oils contain different types of long-chain fatty acids. Special processes are required if the oil or fat contains significant amounts of FFAs. The used cooking oils normally contain 2%–7% FFAs and animal fats contain 5%–30% FFAs. Some very low-quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to these feedstocks, the FFAs react with the catalyst to form soap and water as shown in the reaction Eq. (4.7).



When FFA is lower than about 5%, the reaction can be catalyzed with an alkali catalyst; but an additional catalyst is required to compensate for the catalyst lost in soap formation. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. But, in the case of the FFA level above 5%, the soap hinders the separation of the glycerol from the methyl esters and contributes to emulsion formation during the water wash. To overcome this problem, an acid catalyst such as sulfuric acid (H_2SO_4) can be used to esterify the FFAs to methyl esters as given by Eq. (4.8).



The pretreatment process is used to convert the FFAs to methyl esters and thereby this reduces the FFA level. The schematic representation of the pretreatment process for FFA feedstocks is shown in Fig. 4.8. The FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters (Keim, 1945).

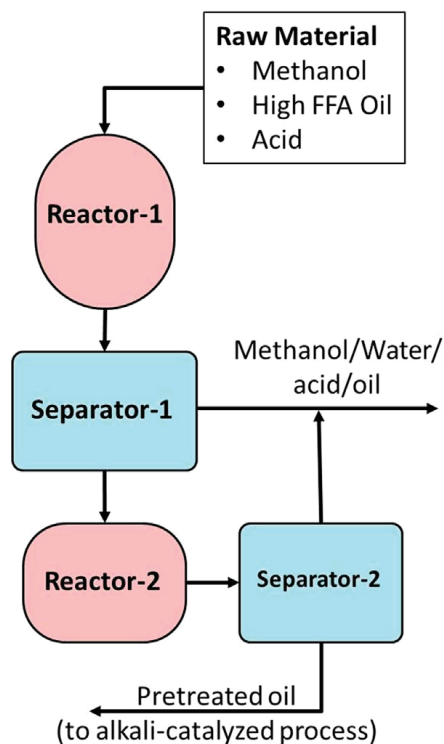


Figure 4.8 Pretreatment process for free fatty acid feedstocks.

4.2.1.2 Alkali-catalyzed transesterification

Alkali catalyst, also known as lye, is a metal hydroxide traditionally obtained by leaching wood ashes, or a strong alkali that is highly soluble in water-producing caustic basic solutions. The lye most commonly refers to NaOH, but historically has been used for KOH. Alkali catalysts such as NaOH, KOH, CH_3ONa , and CH_3OK are used for biodiesel production. However, alkali metal alkoxides are found to be more active than hydroxides (Faruque et al., 2020; Rizwanul Fattah et al., 2020; Sharma et al., 2008). NaOH is used as an alkaline catalyst for the transesterification process because it is cheaper and reacts faster than acid catalysts.

4.2.1.3 Acid- and alkali-catalyzed two-step transesterification

In case of high FFA presence in the bio-oils, the single-stage esterification is not sufficient and double-stage esterification is required. For the preparation of biodiesel, that is, neem methyl ester (NME), the neem oil is used as base raw material and other reactants like methanol-concentrated sulfuric acid and alkaline catalyst KOH are used for the transesterification process. The neem oil has high FFA; therefore biodiesel is produced by processing the neem oil in two stages. For increasing the recovery of biodiesel from feedstocks with high FFA, transesterification with acid as a catalyst is done as the primary treatment. The oil is preheated to about 100°C for 10 min in a cylindrical stainless steel tank (biodiesel reactor) to remove water contents. After cooling to 60°C , a mixture of 400 mL methanol with 5 mL concentrated sulfuric acid (anhydrous) is mixed with 1 L neem oil in the reactor and stirred for half an hour maintaining the temperature at about 60°C . Then the mixture is removed from the reactor and poured in a separating flask and allowed to settle down for 24 h.

The biodiesel settled at bottom of the flask is drained away from the flask to separate this from the glycerol. Thereafter, FFA analysis of biodiesel sampled from the first esterification is done by titration method carried out with phenolphthalein dye and 0.10% of caustic lye (NaOH solution) as a neutralizer. The FFA found was still high, higher than 2.5%. The biodiesel was obtained from the first stage, then further processed with an alkali catalyst. CH_3OK is prepared by mixing methanol (200 mL) and KOH (5–10 mg). Then CH_3OK is added to the preheated neem biodiesel (NB), received from the first stage, in the reactor and the process is done similarly as above for the first stage, and then transesterified NB is separated. The overall NB yield of 88% was reported (Salvi & Jindal, 2020). Thangaraj et al. (2014) reported the maximum yield of 85% biodiesel by using a 1:8 molar ratio of oil to methanol with 0.08% volume of an acid catalyst and 1% of NaOH catalyst at 60°C by two-step reaction processes.

The homogeneous catalysts are more effective, but they can create severe contamination problems that require better separation and product purification methods. This may turn into elevated biodiesel production costs as well as raw material costs.

4.2.2 Heterogeneous catalytic transesterification

Catalysts with different phases like liquid and solid mixture or solid and liquid mixture are termed heterogeneous catalysts. Heterogeneous (solid) catalyst, either acid or base type, is eco-friendly with a good quality yield of biodiesel (Ajala et al., 2020). When compared the heterogeneous catalysts with homogeneous catalysts, it is stated that the heterogeneous catalysts are considered a better option for biodiesel production in the near future. The heterogeneous catalysts can be effectively recycled, recovered, and possess environmentally benign behaviors. Some of the heterogeneous catalysts can execute simultaneous esterification of FFAs and transesterification of the triglycerides available within the non-edible oil effectively (Faruque et al., 2020). The recent developments in heterogeneous catalysts offer the benefits in terms of easy recovery, regeneration, and reuse, as well as immobilized lipases with increased stability and resistance to alcohol denaturation for future industrial use (Toldrá-Reig et al., 2020). The transesterification with alkaline catalysis is preferred at industrial plants producing biodiesel.

4.2.2.1 Solid catalyst

NaOH is used in transesterification reactions due to its high purity and low cost; in addition, a relatively low quantity is needed as compared to KOH (Thangaraj et al., 2019). Strong alkali catalysts such as NaOH, KOH, CH_3ONa , and CH_3OK are used for biodiesel production. Endalew et al. (2011) reported CaO and Li-CaO as solid-phase catalysts for esterification and transesterification of *Jatropha curcas* oil into biodiesel. The solids catalysts include MgO, CaO, Al-Mg hydrotalcite, La_2O_3 , ZnO, CeO_2 , CaCO_3 , sulfated zirconium oxide, sulfated tin oxide, etc. (Rahimpour, 2015; Sua & Guo, 2014). Solid acid catalysts such as aluminosilicates and zeolites are used for catalytic cracking (Pandey et al., 2015).

4.2.2.2 Acid solid catalysts

Acid solid catalysts are eco-friendly and can be used as replacements for liquid acids. The use of solid acid catalyst enables a separation of the product by filtration alone. Generally, the metal oxide solid supports, such as aluminas and silica–aluminas, are used in solid acid catalysts (Worstell, 2014). The prime characteristics of solid acid catalysts can be modified in an economical and eco-friendly way to reduce the overall cost of fuel products on an industrial scale (Parangi & Mishra, 2020).

Over the period of utilization of solid acid catalysts, they suffer from poisoning. Catalysts comprising a metal deposited on a metal oxide solid support experience poisoning and pore surface area reduction. This phenomenon is often called pore plugging “fouling.” So the poisoning of the catalyst reduces the productivity of solid-supported catalysts. Ultimately reaching a point at which the biodiesel produced by the catalyst does not cover the cost of operating the process. In such cases, the solid-supported catalyst in the fixed-bed reactor must be dumped and fresh solid-supported

catalyst is charged to the reactor or the solid-supported catalyst in the fixed-bed reactor must be regenerated (Worstell, 2014).

4.2.2.3 Base solid catalyst

Base catalysts are exclusively suitable for good purity oils with low FFA contents because they are more vigorous than acids in transesterification. Continuous flow and a packed bed arrangement are generally employed for synthesizing biodiesel using a solid base catalyst, which finally facilitates both coproduction of glycerol with good purity and catalyst separation. Therefore this reduces the production cost and promotes the use of the catalyst again. There are various solid base catalysts including alkali metals, alkali or alkaline earth oxides, basic zeolites, immobilized organic bases, and clays such as hydrotalcite (Ono & Baba, 1997).

Solid bases are generally the solids with the Brønsted basic and Lewis basic activity centers that can provide electrons (or accept protons) for (or from) reactants. The usually studied solid material-based catalysts include hydrotalcite, metal oxides, metallic salt, supported base catalyst, and zeolites. Basic solid catalysts such as ZnO, CuO, zeolites, CaO, SrO, MgO, BaO, basic polymers, and carbonates such as MgCO₃, CaCO₃, BaCO₃, A common, and SrCO₃ are some of the heterogeneous transesterification catalysts (Faruque et al., 2020). The summary of commonly used basic materials as solid catalysts for transesterification reactions is shown in Table 4.1 in increasing order of biodiesel yield (Cho & Seo, 2010; Encinar et al., 2010; Guo et al., 2010; Liu et al., 2010; Ngamcharussrivichai et al., 2010; Verziu et al., 2011; Zabeti et al., 2010).

Table 4.1 Summary of commonly used basic materials as solid catalysts for transesterification reactions.

Catalyst	Feedstock	Optimum reaction conditions				Biodiesel yield, %
		Temperature, °C	Time, h	Methanol/oil	Catalyst amount, wt. %	
CaO	Sunflower oil	80	5.5	6:1	1.0	91
CaO/F ₃ O ₄	<i>Jatropha curcas</i> oil	70	1.3	15:1	2.0	95
CaO from egg shells	Palm oil	65	2.0	12:1	1.5	98
Dolomite	Palm kernel oil	60	3.0	30:1	6.0	98
KNO ₃ /CaO	Rapeseed oil	65	3.0	6:1	1.0	98
CaO/Al ₂ O ₃	Palm Oil	64.3	5.0	12.14:1	5.97	98.64
Sodium silicate	Soybean oil	60	1.0	7.5:1	3.0	100

Even if transesterification is workable with catalysts of a base, the general homogeneous base-catalyzed procedure involves several restrictions, which results in increased production expenses anticipated for biodiesel. The uncompromising feedstock provisions are a major concern with this procedure. The FFA content in the lipid feedstock should not exceed 0.5 wt.%, as the higher FFA content causes soap creation. This ultimately hampers fuel-grade biodiesel production (Faruque et al., 2020).

4.2.2.4 Acid–base solid catalysts or bi-functional catalysts

For biodiesel production, the raw material and a base catalyst are required for the transesterification process. In the case of low-grade oil feedstock, an acid catalyst is required to esterify the oil feedstock to reduce the FFA content before the transesterification process during the production of biodiesel. So, there is a need for a bi-functional catalyst, which should possess the acid as well as base catalysis functionality. The bi-functional catalyst has the capability to do both simultaneous esterification of FFA and transesterification of the triglycerides available in the oil. The bi-functional catalyst possesses both active acid and base sites on its surface; therefore it cannot be affected by the present water content or produced water content during biodiesel production. Fig. 4.9 shows the common mechanism for simultaneous esterification and transesterification reactions on a bi-functional heterogeneous catalyst (Faruque et al., 2020; Omar & Amin, 2011; Rahman et al., 2019).

4.2.2.5 Waste material-based heterogeneous catalysts

The preparation of heterogeneous catalysts from both biological resources and industrial waste has received attention due to their low cost and good effectiveness (Faruque et al., 2020). Deka and Basumatary (2011) obtained a new catalyst from the trunk of *Musa balbisiana* Colla (one variety of banana plants) and utilized that for the conversion of *Thevetia peruviana* seed oil to biodiesel. They achieved 96% conversion of oil to biodiesel using 20 wt.% catalysts while maintaining a 3-h reaction time at 32°C temperature. Marwaha et al. (2018) in a review work reported that the large availability of calcium-rich waste materials and their corresponding high catalytic activity in the transesterification of oil is attracting the attention of scientists for the development of heterogeneous catalysts. These are being eco-friendly and cost-effective. Heterogeneous catalysts with high activity can be produced from Ca-based waste materials when calcined at high temperatures. Industrial wastes (red mud, slag, ash) and biological catalysts (chicken egg shells, mollusk shells, animal bones) possess enormous potential towards developing an economical catalyst and subsequently, low-cost biodiesel generation. Alternatively, solid waste can be recycled as a potential substitute for some chemical substances. The developments in solid waste-derived heterogeneous catalysts (e.g., supported and Cu-, Co-, Mn-, Fe-, and Ca-based) for organic contaminant removal and biodiesel production were reported by Wang et al. (2020). General steps in the development of heterogeneous catalysts from waste materials are shown in Fig. 4.10.

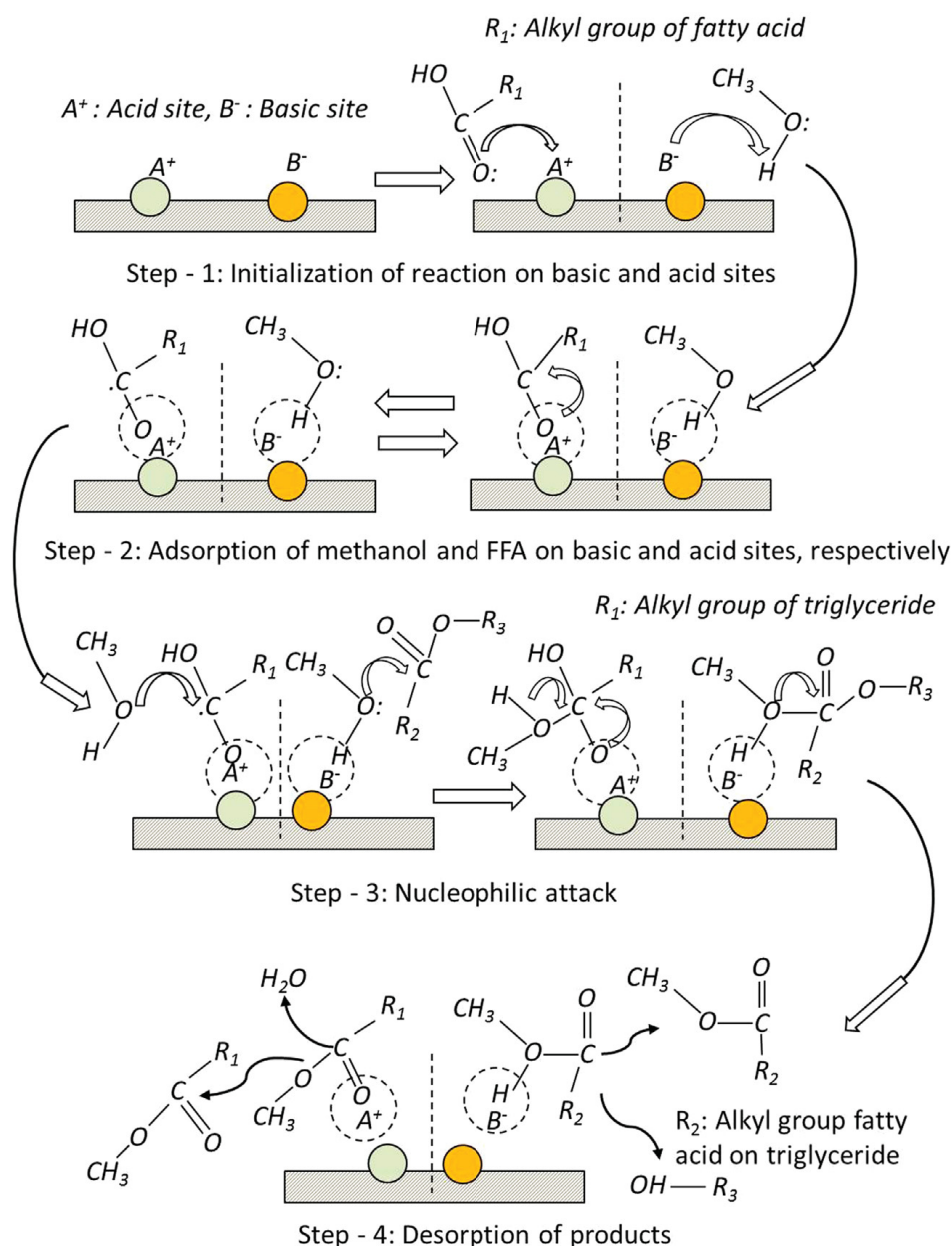


Figure 4.9 Common mechanism for simultaneous esterification and transesterification reactions on a bi-functional heterogeneous catalyst. From Faruque, M., Razzak, S., & Hossain, M. (2020). *Application of heterogeneous catalysts for biodiesel production from microalgal oil—A review*. Catalysts, 10, 1025. <https://doi.org/10.3390/catal10091025>.

The waste material-based heterogeneous catalyst formation from various feedstocks and raw material for transesterification are shown in Table 4.2 (Boro et al., 2011; Deka & Basumatary, 2011; Wei et al., 2009). It is found that catalysts produced from different sources result in a varying yield of the biodiesel and their operating

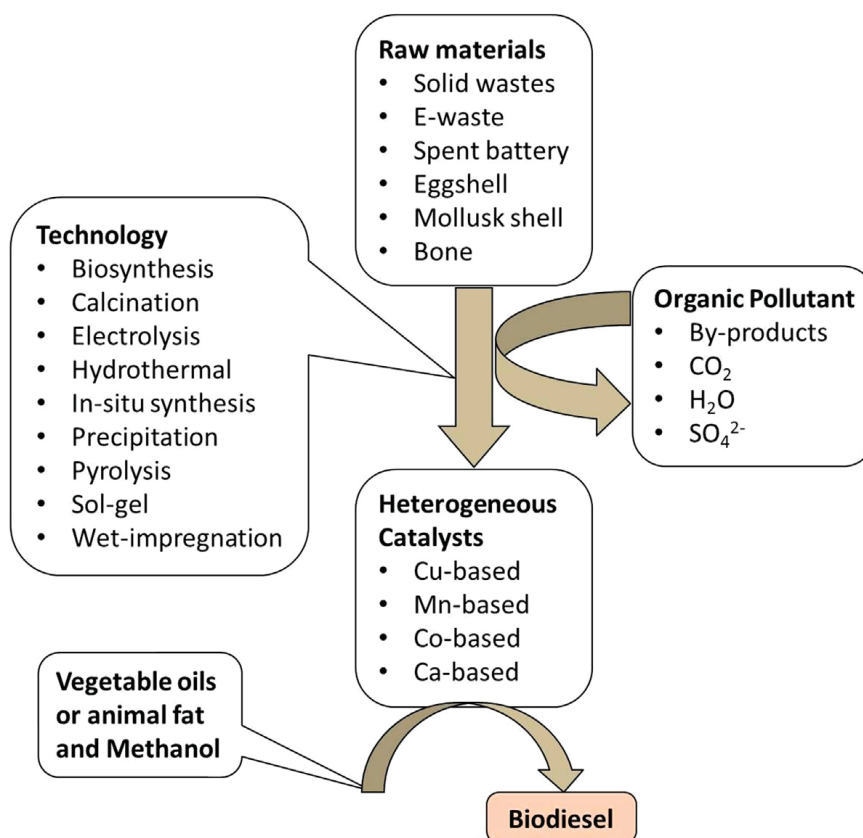


Figure 4.10 General steps in the development of heterogeneous catalyst from waste materials.

conditions are also significantly varying. Therefore, for biodiesel production from different raw materials by using the different catalysts, a parametric optimization of the catalysts and the raw material is required.

4.2.3 Precursor techniques

The precursor method involves atomic-level mixing by forming a solid compound (precursor) in which the metals of the desired compound are present in the proper stoichiometry. The use of low-cost catalysts is one of the main focuses of biodiesel production. Hassan et al. (2018) in their research work prepared the catalysts from calcium oxide (CaO-X) by sol-gel method at different Ca^{2+} precursor concentrations ($X = 1.0, 1.5, 2.0$ M). They reported that 2.0 M of calcium precursor has high catalytic activity and 81% FAME yield was obtained within 3 h reaction.

Rahman et al. (2019) carried out a study on tailoring the surface area and the acid-base properties of ZrO_2 for biodiesel production from *Nannochloropsis* sp. and prepared the catalysts by using surfactant-assisted sol-gel method followed by hydrothermal treatment. They reported that the zirconyl precursor solution is naturally acidic ($\text{pH} < 1$). Under acidic conditions, hydrolysis occurs at a faster rate than

Table 4.2 Waste material-based heterogeneous catalysts.

Serial No.	Sources of catalyst production	Raw material for biodiesel	Results
1.	Trunk of <i>Musa balbisiana</i> Colla (one variety of banana plant)	<i>Thevetia peruviana</i> seed oil	Achieved 96% conversion of oil to biodiesel using 20 wt.% catalyst while maintaining a 3-h reaction time at 32°C temperature.
2.	Waste shells of <i>Turbonilla striatula</i>	Mustard oil	The catalyst from the shells and solid CaO formed at 800°C, about 93.3% biodiesel yield was achieved from the transesterification of mustard oil using 3 wt.% catalyst maintaining 9:1 methanol to oil ratio for a 6-h reaction time at 65°C ± 5°C temperature.
3.	Waste egg shells	Soybean oil	The transesterification of soybean oil with 9:1 methanol to oil molar ratio using 3 wt.% catalyst and maintaining the reaction temperature at 65°C for 3 h. Biodiesel yield more than 95% and used effectively for 13 cycles.

Source: From Boro, J., Thakur, A. J., & Deka, D. (2011). Solid oxide derived from waste shells of *Turbonilla striatula* as a renewable catalyst for biodiesel production. *Fuel Processing Technology*, 92(10), 2061–2067. <https://doi.org/10.1016/j.fuproc.2011.06.008>.

condensation and results in a weak branched gel. The addition of ammonia increases the pH of the solution and the condensation accelerates compared to hydrolysis, thus forming a rigid gel. The developed provides a large number of pores with a high pore volume of ZrO₂. The steps for the development of precursor-based catalysts are shown in Fig. 4.11 (Rahman et al., 2019).

4.2.4 Reactive extraction process

The production of biodiesel through conventional processes involves oil extraction, refining, and transesterification. On the other hand, transesterification can be performed directly from the oil-bearing materials without prior extraction. This route which is often termed “reactive extraction” or “in situ transesterification” has the advantages of simplifying the biodiesel production process as well as potentially reducing production cost. The catalyst concentration, temperature, and particle size mainly affect the rate of ester formation, while the equilibrium yield largely depends on the solvent to oil molar ratio. The general reactive extraction process of biodiesel

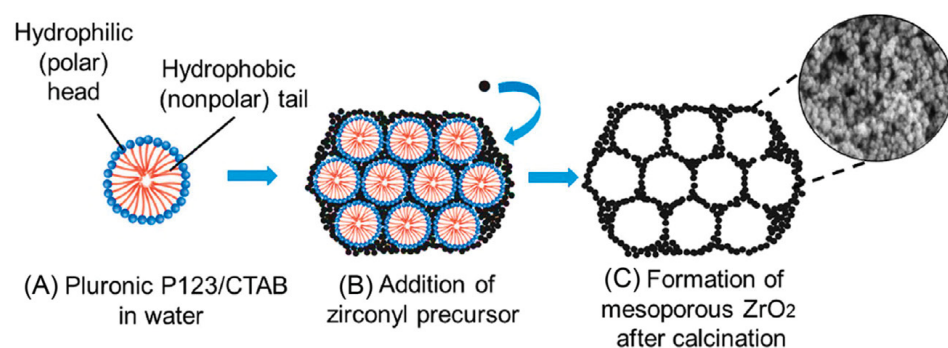


Figure 4.11 Heterogeneous catalyst production from waste materials (A) Pluronic P123/CTAB in water, (B) addition of zirconyl precursor, and (C) formation of mesoporous ZrO_2 after calcination. From Rahman, N., Ramli, A., Jumbri, K., & Uemura, Y. (2019). Tailoring the surface area and the acid–base properties of ZrO_2 for biodiesel production from *Nannochloropsis* sp. Scientific Reports, 9, 16223. <https://doi.org/10.1038/s41598-019-52771-9>.

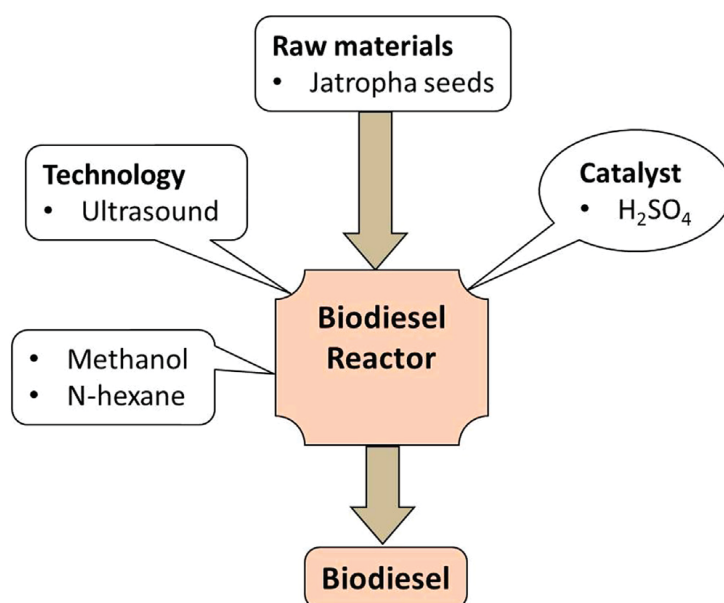


Figure 4.12 Reactive extraction process of biodiesel production.

production is shown in Fig. 4.12. Zakaria and Harvey (2012) reported that from the reactive extraction process the high yield of ester ($> 85\%$) can only be achieved at a high solvent to oil molar ratios ($> 47.5:1$). They also reported that reactive extraction occurs by transesterification of the oil inside the seed, followed by diffusion of the products into the bulk solvent. Tan et al. (2019) carried out the study using a two-step catalytic reactive extraction and the transesterification process was adopted to synthesize biodiesel from solid *Jatropha* seeds, directly using ultrasound irradiation. They reported an extraction efficiency of about $84.0\% \pm 0.5\%$ for the reactive extraction process coupled with ultrasound.

4.3 Biological method

The biological method of biodiesel production utilizes the biocatalysts such as lipase. The biocatalysts can overcome the demerits of the chemical catalytic system. Biocatalysts consist of free lipase, traditionally immobilized lipase (lipase immobilized on nonmagnetic material), and lipase immobilized on magnetic nanoparticles (Thangaraj et al., 2019).

So far, biological catalysis has not been used for commercial production of biodiesel, but experimental results from the laboratory show that it could have distinct advantages over the inorganic route, particularly with regard to purification and related energy savings (Harding et al., 2008). The lipases have the capability to catalyze both transesterifications of triglycerides and hydrolysis in moderate conditions. These are being utilized as a major enzyme during transesterification because they are cost-effective (Gonçalves et al., 1996; Høge-Jensen et al., 1988; Oliveira et al., 1997). The life cycle analysis shows that the enzymatic production route is environmentally more favorable for biodiesel production. It is found that global warming, acidification, and photochemical oxidation are reduced by 5% (Harding et al., 2008).

4.3.1 Enzymatic-catalyzed transesterification

The transesterification of oils having high FFA using a basic catalyst has saponification problems, which can be reduced by using the enzymatic transesterification process. The enzymatic transesterification reaction is similar to conventional transesterification, except that they are catalyzed by a variety of biological catalysts rather than chemical catalysts. Enzymes can be reused as catalysts by being immobilized on solid supports and supplied with a new frame of opportunity. There are different techniques for enzymatic immobilization such as crosslinking, covalent bonding, and microencapsulation. The enzymatic transesterification can be cost-effective as it acts at a neutral pH with a lower reaction temperature as well as creating only a small amount of soap (Faruque et al., 2020). Fig. 4.13 shows the crucial parameters, which could affect the biodiesel yield in enzymatic synthesis (Antczak et al., 2009).

Christian et al. (2019) developed a biocatalyst from *Tamarindus indica* fruit shell ash and used it for biodiesel production. The catalyst had a basic strength greater than 9.7 and a mesoporous structure with a pore size of 3.2 nm. The catalyst used with *Parinari curatellifolia* seeds oil in the optimal conditions of 1:9 methanol to oil molar ratio, with 5 wt.% catalyst loading, 2 h reaction time, 60°C reaction temperature, and 3000 rpm stirring rate. A maximum biodiesel yield of 96.2% was found. The catalyst could be easily separated and subsequently reused for four runs in biodiesel production. The catalyst produced from tamarind fruit shell is very encouraging for the production of biodiesel due to its high performance, low cost, easy preparation, and availability (Christian et al., 2019).

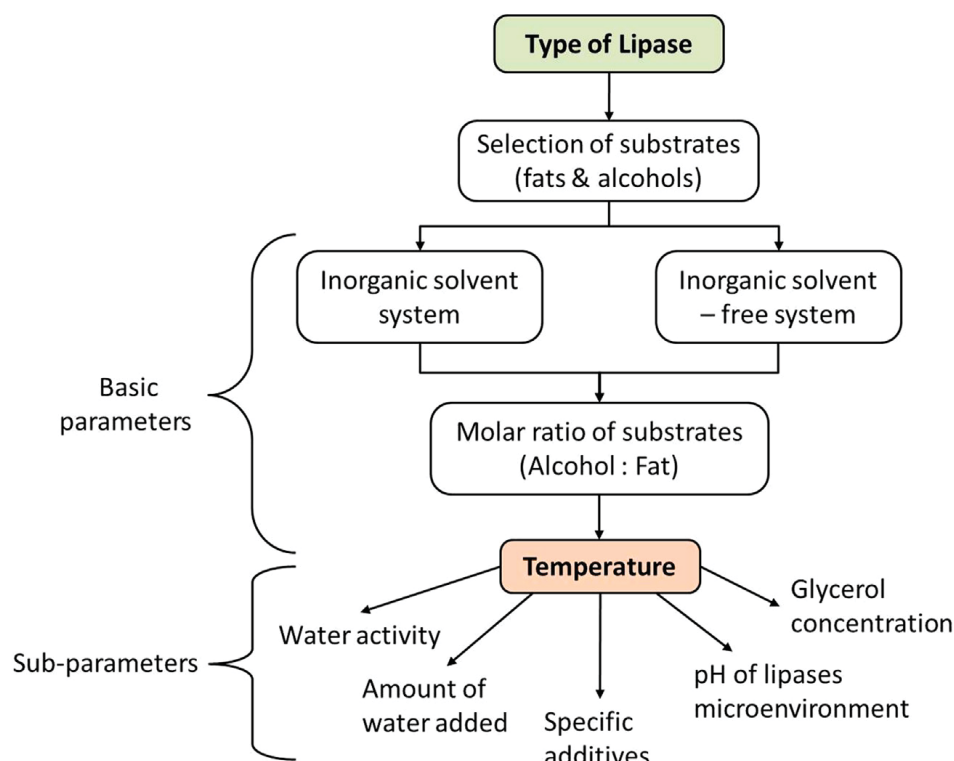


Figure 4.13 Crucial parameters affecting the biodiesel yield in enzymatic synthesis. From Antczak, M. S., Kubiak, A., Antczak, T., & Bielecki, S. (2009). *Enzymatic biodiesel synthesis - Key factors affecting efficiency of the process*. *Renewable Energy*, 34(5), 1185–1194. <https://doi.org/10.1016/j.renene.2008.11.013>.

Arumugam and Ponnusami (2017) carried out a study on waste sardine oil, a by-product of the fish industry, for the production of biodiesel by using lipase enzyme immobilized on activated carbon. Process variables, namely, reaction temperature, water content, and oil to methanol molar ratio were optimized. They reported the ethanol to oil molar ratio of 9:1 as optimum. The reusability of immobilized lipase was reported as five cycles of reuse, then after there was about a 13% drop in FAME yield.

Bhangu et al. (2017) carried out the study on the enzymatic transesterification reaction in a glass cell using a mixture of canola oil, methanol (molar ratio of methanol to oil was 5:1), and lipase under the influence of ultrasound. They prepared the lipase from *Candida rugosa* in an aqueous sodium phosphate buffer (100 mM) solution at pH 7. The ultrasonic horn was inserted into the reaction mixture to provide sonication. It was reported that ultrasonication is an encouraging and effective technique for biodiesel synthesis.

4.3.2 Whole-cell biocatalyst

The use of whole cells has emerged as a useful strategy with several advantages over isolated enzymes. Research in the development of sustainable bio-based processes for

the production of fuels is increasingly attractive due to increased concern for the environment (Garzón-Posse et al., 2018; Lin & Tao, 2017). For any catalytic process, the catalyst's costs and stabilities are of utmost relevance for the economic application in chemical manufacturing (Wachtmeister & Rother, 2016).

To avoid lipase deactivation by methanol in the enzymatic transesterification process, Zhou et al. (2015) developed a two-step biocatalytic process for biodiesel production from unrefined *Jatropha* oil. The unrefined *Jatropha* oil was first hydrolyzed to FFAs by the commercial enzyme *C. rugosa* lipase. They reported maximum yield of FFAs 90.3% at 40°C, water/oil ratio 0.75:1 (v/v), and lipase content 2% (w/w) after 8 h reaction. After hydrolysis, the FFAs were separated and converted to biodiesel by using *Rhizopus oryzae* IFO4697 cells immobilized within biomass support particles as a whole-cell biocatalyst (WCB) (Zhou et al., 2015).

Liu et al. (2010) reported that the *Pichia pastoris* WCB is a promising biocatalyst for biodiesel production in a relatively cost-effective manner (Cho & Seo, 2010; Encinar et al., 2010; Guo et al., 2010; Ngamcharussrivichai et al., 2010; Verziu et al., 2011; Zabeti et al., 2010). Additionally, the resulting enzymatic process may provide a potential method for biodiesel production at an industrial scale. The actinobacteria is a type of WCB, which has direct involvement in biofuel production and plays a significant role in detoxifying fuel-associated toxic compounds. Starting from formation to maturation, microorganisms have been in contact with crude oil in different reservoirs, which contribute to their adaptation to use and modify nearly all chemical categories in crude oil (Anteneh & Franco, 2019; Mohamed et al., 2015).

The use of microorganisms, such as *Escherichia coli*, as WCBs, is a convenient strategy to provide pre-immobilized enzymes. The enzyme acts in the natural cellular environment, which also protects the enzyme from destabilization and degradation. It avoids further laborious production and purification steps and allows repeated use in sequential reactions (Creative-enzymes, 2021). As compared to chemical processes, the WCBs offer several advantages including high selectivity, catalytic efficiency, milder operational conditions, and low impact on the environment (Anteneh & Franco, 2019). The novel process, combining the advantages of enzyme and whole-cell catalysts, saved the consumption of commercial enzymes and avoid enzyme deactivation by methanol (Zhou et al., 2015).

4.4 Supercritical fluid techniques of transesterification

The supercritical fluid (SCF) technique of transesterification of vegetable oil(s) is one of the biodiesel production methods where the process is performed without using any catalyst. This is also called the non-catalytic process of biodiesel production. Generally, transesterification reaction for biodiesel production occurs at reactor temperature 60°C–70°C. When reactor temperature is maintained at a higher temperature ranging from 200°C in

sub-critical temperature to 500°C at the supercritical state, then this method is known as the SCF technique of transesterification. In a study, the reaction temperature of 350°C was considered as the best condition, with a molar ratio of 42:1 of methanol in rapeseed oil (Kusdiana & Saka, 2001). Demirbas (2005) reported that supercritical methanol has a high potential for both transesterifications of triglycerides and methyl esterification of FFAs to methyl esters. The major variables affecting the methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Demirbas (2006) worked on the supercritical methanol technique of the transesterification process and reported the yield of conversion up to 95% in 10 min. Demirbas (2008) also reported that the catalytic supercritical methanol transesterification method is very promising and the yield of conversion rises to 60%–90% for the first 1 min. As compared with conventional biofuel production methods, the SCF technology holds a number of advantages that include fast kinetics, high fuel production rate, ease of continuous operation, and elimination of the requirement of catalysts (Wen et al., 2009).

4.5 Materials, reagents, and equipment

4.5.1 Fatty oils for biodiesel production

Raw material for biodiesel production includes any fatty oil either edible or non-edible and tallows. Initially, biodiesel was produced from edible oils and later on from non-edible oils as raw material. The non-edible vegetable oils such as castor oil (*Ricinus communis*) (Shrirame et al., 2011), linseed oil (Jindal & Salvi, 2012), cottonseed oil (*Gossypium hirsutum*), Jatropha oil (*Jatropha curcas* L.), Jojoba oil (*Simmondsia chinensis*), Karanja seed (*Pongamia pinnata*) (Lahane & Subramanian, 2015), neem oil (Salvi & Jindal, 2020), etc. are the major sources of the raw material for biodiesel production. The tallow, a kind of fat produced from animal bones is also a potential source of raw material for biodiesel (Barik & Vijayaraghavan, 2020; Bhatti et al., 2008; Toldrá-Reig et al., 2020). Based on feedstocks, biodiesel is categorized as first generation, second generation, and third generation (Fig. 4.14) (Aransiola et al., 2014; Faruque et al., 2020; Jindal & Salvi, 2012).

Microalgae have been considered as third-generation most prospective feedstock for biodiesel production. The microalgae are minute photosynthetic organisms that are widely located in wide-ranging ecological settings, on water and land. The microalgae have a high return in terms of lipid content (Zhang et al., 2014), but their biodiesel yield significantly varies among the various microalgae species (Mata et al., 2010).

4.5.2 Reagents required for biodiesel production

Methanol: Methanol is toxic and must be handled and used in a well-ventilated area. Inhalation or ingestion of methanol can be very harmful at higher concentrations and

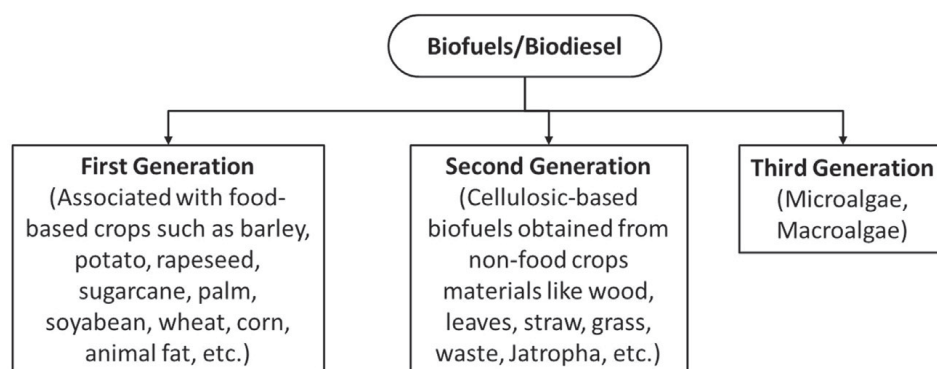


Figure 4.14 Feedstock and generation of biodiesels. From Faruque, M., Razzak, S., & Hossain, M. (2020). Application of heterogeneous catalysts for biodiesel production from microalgal oil—A review. *Catalysts*, 10, 1025. <https://doi.org/10.3390/catal10091025>.

can lead to death or blindness. It is especially damaging to the eyes; safety goggles, chemical-resistant clothing, and gloves must be worn whenever handling the material. If concentrations in the air exceed 200 ppm, air-supplied respirators are required, preferably with a full-face mask. The level at which the odor of methanol is perceptible is greater than 200 ppm. Thus if one “smells” methanol in the processing facility, unhealthy personal exposure is already occurring. There have been many instances where methanol was swallowed purposely, because of its mildly intoxicating effect (much like ethanol). Consumption has led to numerous cases of death or blindness, and precautions must be taken to keep this chemical away from children and animals.

Methanol consumption, inhalation of high concentrations, and any contact with the eyes require immediate medical attention. Short-term exposure to methanol vapor can irritate the eyes, nose, and throat, and cause headache, nausea, vomiting, dizziness, and trouble breathing. Other common symptoms of drunkenness, such as lightheadedness, giddiness, blurred vision, and dilated pupils, might also appear. The symptoms depend on the level and length of exposure and can vary from person to person. Methanol readily dissolves into water and if released without proper treatment, can get into the water table. Methanol is flammable and presents a fire hazard. Its vapors are heavier than air and can travel a substantial distance to find an ignition source with a subsequent flashback to the processing unit or methanol storage tank. Methanol’s flash point is a rather low 11°C, which is the point whereby sufficient vapor is released to form a flammable mixture. At biodiesel processing temperatures (60°C–80°C), there is enough methanol vapor generated to sustain a serious fire, if the air is allowed to mix with the methanol and there is no sparking available.

NaOH and KOH: Both are corrosive and may be fatal if ingested. These chemicals are both referred to as “lye” or “catalyst.” Skin contact can cause severe burns and the area affected should be thoroughly flushed with water or a dilute vinegar solution. Inhalation of the solid NaOH or KOH is possible if the material is reduced to

dust-sized particles. Any of these situations is critical, requiring immediate medical attention. NaOH and KOH must be stored away from water since water will inhibit the biodiesel reaction as well as cause heat release due to mixing, which can potentially cause a fire in adjacent material. NaOH, KOH, and concentrated solutions should never contact aluminum as they will create explosive hydrogen gas.

When measuring anything but very small quantities of NaOH or KOH, it is very important to wear a dust mask or cartridge respirator to prevent inhalation of caustic particles. A spray bottle of vinegar is handy for neutralizing any small residual catalyst spills in the workplace. Fine particles of NaOH or KOH will produce holes in clothing; thus a protective apron or jumpsuit is also advised. It is also helpful for each person working in the biodiesel shop to keep a spare change of clothes on hand so that accidentally contaminated clothing can be quickly shed if needed.

CH_3ONa is made by combining methanol and NaOH. CH_3OK is made by combining methanol with KOH. These mixtures have many of the same corrosive and toxic characteristics as their components and should be handled similarly. In solid form, CH_3ONa and CH_3OK are not very stable and should be avoided. They can ignite on contact with water or moist air.

4.5.3 Biodiesel processing equipment

Every production system requires proper equipment and facility. Many of the problems associated with processing biodiesel can be handled with a properly engineered design of processing equipment. There are varieties of biodiesel system designs for the effective conversion of vegetable oil into biodiesel. For safe and energy-efficient production, a closed system that minimizes chances for the escape of methanol vapors into the workspace or environment must be used. Biodiesel reactor is subjected to the reactive mixture at comparatively high temperature. Therefore the material of the biodiesel reactor should be inert to chemicals (i.e., acid, base) and should sustain high temperature and good strength. The biodiesel reactors are made of stainless steel, ceramic, and glass materials.

Batch processing biodiesel reactor: In the case of batch processing of biodiesel at the laboratory level, single reactors are used. The single reactors with 1-, 5-, 10-, 20-, and 50-L capacity are designed. A single reactor system at the laboratory scale is shown in Fig. 4.7. It consists of a reactor, heating plate with a magnetic stirrer, reflux type condenser, and stand.

Magnetic stirrer: A magnetic stirrer is a device widely used in laboratories and consists of a rotating magnet or a stationary electromagnet that creates a rotating magnetic field. This device is used to make a stir bar, immersed in a liquid, quickly spin, or stirring or mixing a solution (Fig. 4.15).



Figure 4.15 Magnetic stirrer and heating plate.

Continuous production of biodiesel: For continuous production of biodiesel, a large quantity of methanol or mixtures that contain methanol and catalysts is required. In such a case, a closed system, wherein oil, chemicals, and end products can be safely transferred using pumps, tubing, and valves is required. The flow process diagram for continuous production of biodiesel is shown in Fig. 4.16, where various processes are shown and methanol is recycled back to the reactor. The closed reactors must be equipped with a temperature and pressure relief valve that is compatible with the tubing used to plumb the reactor. A manually operated vent valve, plumbed to the outdoors, is also essential. A sealed system based on a metal tank also allows for the recovery of excess methanol from biodiesel fuel and the glycerol by-product, which saves money and reduces handling and environmental complications after processing. When plumbing a reactor of any design, stainless steel tubing should be used wherever possible, as they are most compatible with the chemicals involved in biodiesel processing. Galvanized fittings and any copper parts will reduce the oxidization stability (shelf life) of biodiesel, while standard PVC tends to break down over time.

4.5.4 Steps and protocols for small-scale biodiesel production

There are several alternative methods to successfully transform feedstock oils into biodiesel. This section describes the procedure and regulations for small-scale production of biodiesel. The simplified processing steps are described as follow:

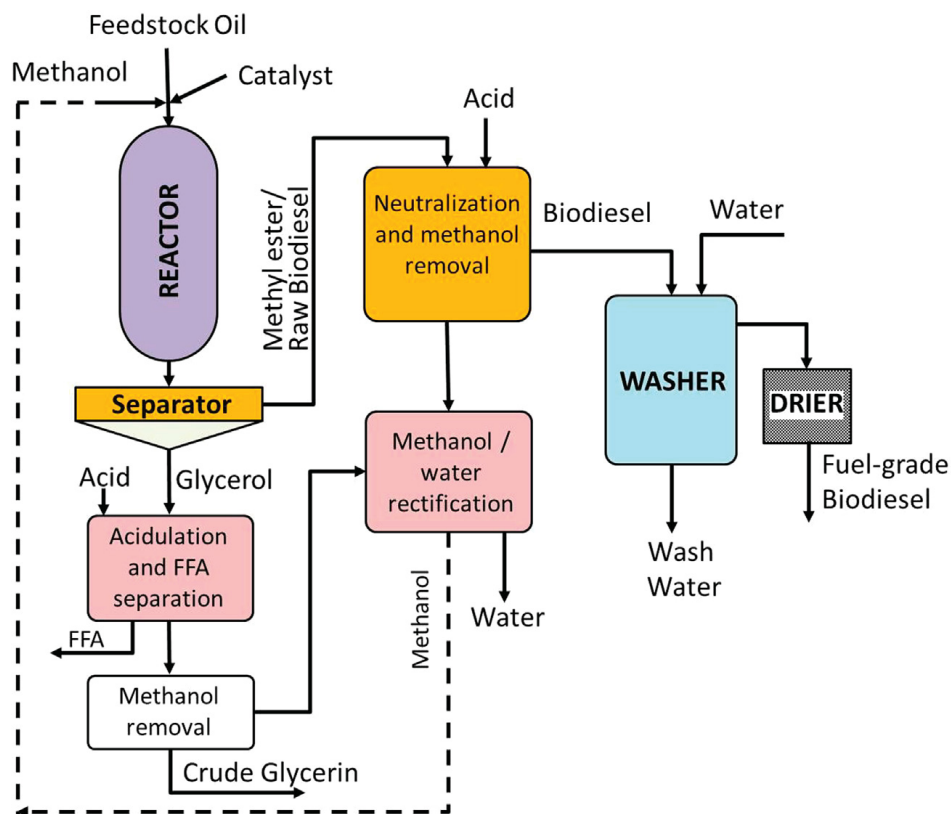


Figure 4.16 Flow process diagram for continuous production of biodiesel.

- Acquire feedstock oil,
- Filter oil to remove particulates,
- Check oil for water content; de-water if needed,
- Test oil for FFA content,
- Make a test batch for the particular feedstock,
- Mix the large batch using the recipe from a successful test batch,
- Maintain accurate detailed records of all variables in each batch of fuel: oil source, mixing time, temperature, quantities of reactants, any other processing variables,
- Drain glycerol by-product and label for further processing, temporary storage, or disposal,
- Recover excess methanol from raw biodiesel,
- Pump biodiesel to wash tanks and wash,
- Pass the washed biodiesel through a drier to remove water from the biodiesel,
- Filter the fuel prior to storage,
- Test fuel for quality parameters,
- Recover methanol from glycerol,
- Dispose glycerol and wash water in a safe and responsible manner.

4.6 The production facility and space

An ideal space for biodiesel production should be well-ventilated yet protected from weather, and lockable to prevent untrained people from accessing chemicals and equipment. Adequate ventilation is absolutely required due to serious health hazards associated with methanol fumes and lye dust. Ventilation can be provided mechanically, via fans or chemical fume hoods, or by working outdoors in the open air. Storage space for vegetable oil, chemicals, and processing gear should be ample and should not cramp the working space. Electrical and water service are also required for most processing systems. A secondary containment system is advisable in case of large spills of oil, biodiesel, wash water, etc.

A “best practice” is to have a separate space dedicated to biodiesel production, apart from other buildings that serve multiple purposes. Biodiesel processing in existing multiuse buildings risks the loss of assets in case of an unforeseen fire or other accident. Users are cautioned to absolutely avoid producing biodiesel in quantity inside their personal residences.

4.7 Analysis and statistics of biodiesel production

Biodiesel is produced from raw materials produced from natural resources, such as oil-seeds of trees and animal fats. The nature or characteristics of the raw material vary widely and therefore, during biodiesel production varieties of combinations of alcohols and catalysts are used. For a different type of raw materials for biodiesel production, the type of catalysts, catalysts concentration, alcohol, molar ratio temperature and reaction time is shown in [Table 4.3 \(Thangarasu & Anand, 2019\)](#).

4.7.1 Fuel quality

The primary criterion for biodiesel quality is adherence to the appropriate standard. Generally, the ASTM D6751-02 standards [i.e., Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels) are used for biodiesel. Commonly, the fuel quality of biodiesel is influenced by several factors:

- The quality of the feedstock.
- The fatty acid composition of the parent vegetable oil or animal fat.
- The production process and the other materials used in this process.
- Post-production parameters.

The fuel quality of biodiesel is decided based on calorific value, viscosity, density, flash point, acid value, ash content, etc. [Table 4.4](#) shows the properties of petro-diesel and biodiesels ([ASTM, 2002](#)).

Biodiesel production or transesterification of fatty oils is carried out through various methods, and different technologies are involved in it. As previously discussed, methods of transesterification such as chemical catalysts, enzymatic catalysis, and SCF

Table 4.3 Production of biodiesel from vegetable oil feedstocks by catalyzed transesterification.

Non-edible oil	Catalysts	Catalyst concentration	Alcohol	Molar ratio	Temperature (°C)	Reaction time (h)	Biodiesel yield (%)
<i>Jatropha curcas</i> L.	H ₂ SO ₄	0.8%	Methanol	9:1	45	2	90–91
	KOH	0.55%–0.7% (w/w)	Methanol	5:1	60	0.24	98–99
	<i>Rhizopus oryzae</i> (RL)	4% (w/w)	Methanol	3:1	30	1	80
	NaOH	0.7%–1% (w/w)	Methanol	3:10 (v/v)	50	2	90.1–98
<i>Calophyllum inophyllum</i> L.	KOH	1.5%	Methanol	6:1	65	4	85
Rice bran	NaOH	0.75% (w/w)	Methanol	9:1	55	1	90.2
<i>Pongamia pinnata</i>	NaOH	1%–1.5% (w/w)	Methanol	6:1	65	0.6–3	90.4
	KOH	1%	Methanol	6:1	65	3	97–98
<i>Azadirachta indica</i>	NaOH	0.6% (w/w)	Methanol	6:1	65	1	83
<i>Hevea brasiliensis</i>	NaOH	1% (w/w)	Methanol	6:1	60	1	84.46
Palm oil	Methoxide	6:1	Methanol	6:1	60	1	88

Source: From Thangarasu, V., & Anand, R. (2019). Comparative evaluation of corrosion behavior of aegle marmelos correa diesel, biodiesel, and their blends on aluminum and mild steel metals. In *Advanced biofuels: applications, technologies and environmental sustainability* (pp. 443–471). Elsevier. <https://doi.org/10.1016/B978-0-08-102791-2.00017-9>.

Table 4.4 Properties of petro-diesel and biodiesels.

Fuel	Density (kg/m ³)	Calorific value (MJ/kg)	Viscosity (cSt)	Flash point (°C)
Diesel as per ASTM D975	830 at 38°C	42.8	3.67 at 38°C	59
Biodiesel as per ASTM D6751	<900 at 38°C	—	<6 at 38°C	>130
Neem biodiesel	870 at 40°C	39.75	6.52 at 40°C	76

Source: From ASTM. (2002). *American Society for Testing and Materials, Standard specification for biodiesel fuel (B100) blend stock for distillate fuels*, Designation D6751-02.

Table 4.5 Transesterification technologies with merits and demerits.

Type of transesterification	Merits	Demerits
Chemical catalysis	Reaction condition can be well controlled Large-scale production The cost of the production process is cheap The methanol produced in the process can be recycled High conversion of the production	Reaction temperature is relatively high, and the process is complex The later disposal process is complex The process needs much energy Needs an installation for methanol recycling The wastewater pollutes the environment
Enzymatic catalysis	Moderate reaction condition A small amount of methanol is required in the reaction Have no pollution to natural environment	Limitation of enzyme in the conversion of short chain of fatty acids Chemicals exist in the process of production are poisonous to enzyme
Supercritical fluid techniques	Easy to be controlled It is safe and fast Friendly to environment	High temperature and high pressure in the reaction condition leads to high cost of production and wastes energy

techniques have various merits and demerits (Quader & Ahmed, 2017). The complied merits and demerits of transesterification technologies are shown in Table 4.5.

4.8 Safety considerations during biodiesel production

Biodiesel is produced from bio-oils by reacting with alcohols in the presence of catalysts. After the separation of raw biodiesel, the remaining glycerol and wastages are to be disposed of properly. Major precautions are necessary to avoid personal poisoning,

fire, and contamination of soil and water resources. Safety should be the top priority in any biodiesel operation, above all other goals. Accidents involving chemicals and/or large volumes of vegetable oil, biodiesel, or by-products can cause injury, loss of life, property damage, or environmental contamination.

4.8.1 Chemical exposure and safety

Methanol and lye are two hazardous chemicals that are required to convert vegetable oil into biodiesel. Methanol presents a significant fire risk and over-exposure can cause neurological damage. Methanol is flammable and a toxic alcohol. Methanol also presents a serious fire risk. The lye is a corrosive and caustic base. The lye can cause skin and lung irritation. Both methanol and lye can cause eye damage or blindness. Therefore most precautions are essential to avoid poisoning, fire, and contamination of soil and water resources ([Farm-Energy, 2020](#)). A comprehensive approach to safety begins with a whole-system consideration of all potential areas for risk, followed by thorough plans for accident prevention. As a backup, preparations should also be made for response to any accident that may occur.

4.8.2 Handling of by-products

Biodiesel production units generate substantial quantities of crude glycerol as a by-product (about 1 gallon of a waste product containing glycerol for every 5 gallons of biodiesel produced). For the purification of raw biodiesel into fuel biodiesel, huge amount of water is required and may generate as much as 3 gallons of wastewater for each gallon of fuel produced. Both glycerol and wastewater require proper handling and disposal consideration.

Free glycerol: After completion of transesterification reaction, the residual mixture contains raw biodiesel, glycerol, water, and methanol. The amount of glycerol that is left in the finished biodiesel is known as free glycerol. The glycerol is essentially insoluble content in the raw biodiesel and can be separated easily by settling or centrifugation and removed. The free glycerol in raw biodiesel may remain either as suspended droplets or as the very small amount that is dissolved in the biodiesel. The alcohols can act as co-solvents to increase the solubility of glycerol in the biodiesel. Most of this glycerol can be removed by the hot water wash process. Fuel with excessive free glycerol will usually have a problem with glycerol settling out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine.

Residual alcohol and residual catalyst: The biodiesel typically contains 2%–4% methanol after the separation, which may constitute as much as 40% of the excess methanol from the reaction ([Knothe et al., 2010](#); [Stidham et al., 2000](#)). The methanol and the alkaline catalysts are more soluble in the polar glycerol phase, and most of that

is removed when the glycerol is separated from the biodiesel. The experimental studies have shown that as little as 1% methanol in the biodiesel can lower the flash point of the biodiesel from 170°C to less than 40°C. Therefore by including a flash point specification of 130°C, the ASTM standard limits the amount of alcohol to a very low level ($<0.1\%$). The lowering of flash points presents a potential safety hazard in the biodiesel as the fuel may need to be treated more like gasoline, which also has a low flash point, than diesel fuel (ASTM, 2002).

Water and sediment: After washing the biodiesel, the water and sediment contaminations are residuals leftover. This requires proper housekeeping and filtration of wastewater for recirculation.

4.8.3 Safety gears during biodiesel production

Proper safety gear for working with NaOH or KOH includes elbow-length gloves, chemical safety goggles, a dust mask or respirator, long pants, and shoes. An eyewash station and/or emergency shower within 25 ft. of the workspace are also highly recommended.

The following safety gears should be on hand each time while preparing biodiesel:

- Chemical-resistant gloves (butyl rubber is best for methanol and lye)
- Chemistry goggles (indirect vented)
- Face shield
- Dust mask or cartridge respirator
- Plumbed eyewash station
- Small spray bottle with vinegar for neutralizing lye spills
- Access to running water
- Calling facility and emergency telephone numbers
- Fire extinguishers
- Absorbent material and spill-containment supplies

4.9 Environmental issues and regulations

Production of biodiesel at laboratory level or pilot level may not be much affecting the environment, but when it is produced at a large scale for commercial needs, always there are some associated by-products or wastes. The product, by-products, and wastes should be managed properly for sustainable power generation. For a better understanding of environmental effects associated with biodiesel production, the researchers commonly use the method of life cycle assessment (LCA). It is very important to understand the life cycle analysis and long-term effects of any technology on environmental components like earth, water, and air. At various stages in a biodiesel's life cycle, there is an associated use of non-renewable resources and generation of emissions. The LCA is defined as an International Standard Organization method aimed to identify pollution transfer from one step to another one, or from one kind of

environmental impact to another one. This approach considers the entire life cycle of a product or the so-called “from cradle to grave” principle (Guinée & Heijungs, 2016; Morales et al., 2019). The LCA is a valuable tool for quantifying the environmental effects of biodiesels, but the selection of proper assessment methods greatly affects the results.

4.9.1 Biodiesel-induced land-use changes

Biodiesel feedstock resources are explored from natural habitat, where carbon is stored in soil and in above-ground and below-ground vegetation. Soil carbon storage depends on soil characteristics and past disturbances. The amount of carbon stored in vegetation depends on the vegetation type. Therefore land-use changes that involve removing or planting of vegetation could either release a large amount of carbon from soil or store carbon depending on the conditions of the land prior to use, crop characteristics (Cho & Seo, 2010; Encinar et al., 2010; Fearnside, 1996; Guo et al., 2010; Liu et al., 2010; Ngamcharussrivichai et al., 2010; Verziu et al., 2011; Woodbury et al., 2006; Zabeti et al., 2010), and farm or land management practices. Similarly, the land-use change could disrupt or enhance the future potential of land to store carbon.

4.9.2 Regulation issues in biodiesel production and utilization

Biodiesel production facilities are subjected to regulation by competent authorities and it may vary from country to country. The objectives are almost similar and dedicated to the safe production and use of biodiesel. Currently, small-scale, non-commercial facilities are exempt from regulating authorities permitting for fuel processing but will be subject to “discretionary enforcement” if problems or complaints arise. The biodiesel fuel quality is assessed with the ASTM D6751-02 standards. The disposal of by-products and commercialization of biodiesel requires permit/certification and controlling regulated by government agencies in specific country.

Certification: Certification is an authority provided by regulating agency for practical implementation of the standard or of the principles and criteria that are aimed for the production of biodiesel and disposal of wastes or by-products. Certification is the practice that implies a third-party assessment of the management procedures with respect to a certain standard (Benenson et al., 2014).

Issues with biodiesel: Biodiesel is gaining popularity in the transportation and power generation sector as fuel for compression ignition engines. But, engine durability is the real challenge of using biodiesel blends as an engine fuel. The oxy-polarity characteristics of esters make the biodiesel a good solvent, which results in degradability of elastomeric seal, including swelling, shrinkage, embrittlement, and changes in physical properties such as hardness and tensile strength. Another issue is high solubility of biodiesel could cause especially fuel system encumbrance (Fontes, 2010).

4.10 Summary

Biodiesel is a sustainable, renewable, and environmentally benign alternative fuel for diesel engines and thermal applications. Biodiesel can be produced from a number of feedstocks including vegetable oils, used cooking oils, animal fats, etc. Biodiesel, that is, the end product in the process of transesterification of the feedstock oil, must meet quality standards for best diesel engine performance. The transesterification of vegetable oil and tallows or algae oil in the presence of methanol using a suitable catalyst are good practices for the production of biodiesel. The transesterification reactions face some challenges related to the presence of FFA in the feedstock. The advancements in efficient and economical catalysts with an environmentally compassionate process are crucial to overcoming the problems associated with biodiesel production.

Biodiesel production at a small scale should be carried out in a safe and environmentally responsible manner that generates a quality product. Some metal oxides provide a high yield of biodiesel under milder conditions and the ability to regenerate. Hence, it is essential to concentrate on this novel approach, due to its promising results. However, supplementary research into the economic viability should be made, before taking into consideration industrial biodiesel production. Staying up to date on process improvements and government regulations is essential.

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