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Biodiesel production via transesterification reaction

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Abstract

Global warming, climate change, local air pollution, ozone depletion, acid rain and depletion of fossil fuel are the major global environmental issues. Presently, non-renewable fossil fuels meet up to 80% of the world's energy demand. Rapid consumption of fossil fuels as well as rising environmental pollution caused by extreme CO_2 emissions, sulphur dioxide, and aromatic hydrocarbons has become crucial in searching for a clean and renewable energy source such as biodiesel. With continuous growth in the world's population, rapid industrialization, urbanization, and economic growth, fossil fuel consumption is escalating to meet the global energy demand. Biodiesel is renewable, non-toxic, environment-friendly and an economically feasible options to tackle the depleting fossil fuels and its negative environmental impact. Biodiesel is an alternative fuel made by transesterification reaction of oil and alcohol under the influence of catalyst. Biodiesel is an alcoholic ester of various fatty acids, also known as FAME (Fatty Acid Methyl Esters). In the process of transesterification, the performance of the catalyst is the key factor of the biodiesel yield. Catalysts used in biodiesel production are classified as homogeneous, heterogeneous, and enzymatic catalysts. The incorporation of a catalysis-based transesterification reaction generally increases the rate of reaction and enhances the yield of the end product. In case of homogeneous catalysts, there are problems of catalyst poisoning and contamination. Heterogeneous acid catalysis has a lesser toxic effect and gives rise to fewer environmental problems compared to the homogeneous mode. The cost of each specific catalyst depends on various factors, including the source, synthesis method, and its reusability. Generally, using waste or biomass as sources of catalysts may reduce the price of commercially available solid catalysts.

Keywords: Biodiesel; Catalyst; Fatty Acid Methyl Esters (FAME); Fossil fuel; Global warming; Non-edible oil; Transesterification; Waste Cooking oil

1. Introduction

Biodiesel is a green biofuel made from renewable biological materials such as vegetable oils, non-edible oils, waist used oils, animal fats and algae [1-85, 110-113]. Non-edible plant oils, waste cooking oils, and edible oil industry by-products are suggested as effective biodiesel feedstocks because non-edible feedstock does not compete with food from human consumption [1-85, 110, 111]. However, nowadays, the major feedstocks of biodiesel are edible oils and this has created food vs fuel debate. Therefore, the future prospect is to use non-edible oils, animal fats, waste oils and algae as feedstock for biodiesel. The primary source for fulfilling basic energy needs is regular non-renewable petroleum-based fuel [1-85, 110, 111-113]. Energy has always been considered as a key source of sustaining the economic growth of any country, and fossil fuels such as coal, natural gas, and crude oil have been contributing as major sources for the fulfilment of this energy need [1-85, 110, 111-113]. However, the depletion of these non-renewable resources, as well as their direct role in environmental problems such as global warming, climate change has moved towards an alternative way of conserving and utilizing energy [1-85, 110, 111-113]. Due to economic development, energy demand has increased with time. Overpopulation, urbanization, and deforestation have laid the foundation for this energy gap [1-85, 110, 111-113]. However, ecosystem has been destroyed by severe environmental concerns such as intensifying local air pollution,

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ozone depletion, acid rain, and global warming [1-85, 110, 111-113]. It is due to the emission of hazardous gases like CO_2, SOx, NOx, CO, and hydrocarbons produced during fossil fuel combustion that cause the greenhouse effect [1-85, 110, 111-113]. Another problem is that due to continuous indiscriminate consumption, overexploitation led to the depletion of natural fossil fuel, resulted in the hiking of petrol and diesel prices [1-85, 110, 111-113]. A great advantage of biodiesel over petroleum fossil fuel is that it has less harmful gas emissions, such as carbon monoxide, sulphur dioxide, and aromatic hydrocarbons [1-85, 110, 111-113]. Biodiesel can be easily used with fossil diesel by blending at any required ratio, and also required zero modification to be used in general diesel engines [1-85, 110. 111-113]. The most common method for biodiesel production is transesterification, in which lipid and low carbon alcohol are commonly used as raw materials, in the presence of a catalyst [1-85, 110, 111-113].

Biodiesel is an alternative fuel made by transesterification reaction of oil and alcohol [8-113]. Biodiesel is an alcoholic ester of various fatty acids, also known as FAME (Fatty Acid Methyl Esters) [1-85, 110, 111-113]. The major components of plant oils and animal fats are triacylglycerol (TAGs); the esters of fatty acids and glycerol [1-85,110-113]. Biodiesel has environmental advantages, such as low levels of carbon dioxide and monoxide emissions, low toxicity and it is biodegradable [1-85, 110-113]. Its main characteristic is that biodiesel has similar properties to conventional diesel, such as viscosity, cetane number, and energy content [1-85, 110-113]. Furthermore, it is possible to blend in any proportion with petroleum-derived diesel [1-113]. Therefore, biodiesel is one of the most common biofuels in the world [1-85, 110-113]. Biodiesel is a renewable fuel, biodegradable, and less polluting than diesel, obtained from the triglycerides transesterification or esterification of free fatty acids (FFA) with short chain alcohol (methyl or ethyl alcohol) [1-85, 110-111-113].

India maintains its biodiesel blending goal target of 5 percent for on-road use by 2030. The national average blend rate remains unchanged at 0.1 percent for 2023 [44]. Due to import restrictions on palm stearin, a disorganized supply chain of used cooking oil (UCO), animal fats, high feedstock costs, and a shortage of supply of palm oil, India's biodiesel usage remains extremely low [44-46]. India maintains an ambitious diesel blending goal (on-road use) target of 5 percent with biodiesel by 2030 [44-46]. According to the Indian government, the national average blend rate has marginally increased from 0.07 percent in 2022 to 0.10 percent in 2023 [44]. India's biodiesel production is primarily produced from animal fats, limited quantities of non-edible oils, UCO, and imported palm oil and palm stearin [44-46]. Biodiesel utilization in India remains exceptionally low due to import limitations, a lack of an organized supply chain, and excessive costs and non-availability of feedstocks [44]. Approximately 3 MMT of UCO are produced annually, but a lack of stable procurement mechanisms results in limited uptake [44-46]. Around 80 percent of biodiesel production expenses stem from feedstock procurement [44-46]. In India, biodiesel is produced primarily from non-edible vegetable oil, acid oils, animal tallow, and palm stearin oil. In the following section, biodiesel feedstocks, the process of transesterification reaction, and role of different catalyst in biodiesel production has been discussed.

2. Biodiesel Feedstocks

Vegetable oils or animal fats are the most used raw material for biodiesel production [1-85, 110, 111-113]. However, recently other raw materials, such as plants (jatropha, castor, neem, and pongamia), macroalgae or microalgae are being considered as a promising alternative and renewable source for biodiesel production [1-85, 110, 111-113]. Many non-edible plant oils have fatty acid composition and physico-chemical properties that enable them to be suitable for biodiesel production as that of edible oils [1-113]. Moreover, many potential non-edible plant oil for biodiesel have been identified, the oil extraction and biodiesel production methods have also been optimized [1-113]. The potential feedstock of biodiesel include, edible and non-edible oils, animal fats, waste oils and algal biomass [1-113]. However, now a days, more than 95% of the world biodiesel is produced from edible oils and this resulted in food versus fuel debates, rising in the price of oil and environmental problems [1-113]. To overcome these problems, it is important to use relatively cheaper and non-edible biodiesel feedstock such as non-edible oils, waste animal fats and waste oils [1-113].

Non edible crops in India as a feedstock for biodiesel production are Karanja (Pongamia) (*Pongamia pinnata*), *Jatropha curcas*, Mahua (*Madhuca longifolia*), Candlenut (*Aleurites moluccanus*), Rubber (*Hevea brasiliensis*), Soapnut (*Sapindus mukorossi*), Jojoba (*Simmondsia chinensis*), Tobacco (*Nicotiana tabacum*), Neem (*Azadirachta indica*), Karanja (*Millettia pinnata*), Rapeseed Moud oil, Castor (*Ricinus communis*), Polanga (*Calophyllum inophyllum* L), Cotton (*Gossypium*), Kusum (*Carthamus tinctorius*), Yellow oleander (*Cascabela thevetia*), Sea mango (*Cerbera odollam*), Tung (*Vernicia fordii*), and Bottle tree (*Brachychiton rupestris*) [1-85, 110, 111-113].

Biodiesel is derived from various sources: microalgae, animal fat, vegetable oil, algae, oils from the fungal origin, terpenes, latex, edible waste oil, or surplus cooking oil from household and commercial practices [1-85, 110, 111-113]. Animal fats include poultry, beef tallow, fish, and pork lard [1-85, 110,111-113]. For many years, edible vegetable oils such as sorghum, sunflower, barley, peanut, oat, and coconut have been used [1-85, 110, 111]. About 17% of total grain produced globally is used to produce biodiesel [1-85, 110, 111-113]. However, due to their competition with food supply-demand, non-edible vegetable oils are preferable feedstock for bio-fuel synthesis [1-85, 110, 111]. Biodiesel feedstock must satisfy two provisions: low production cost and a large production scale [1-85, 110, 111]. Non-edible oil-yielding seed plants, including *Raphanus sativus*, *Raphanus raphanistrum*, *Prunus cerasoids*, and *Lepidium perfoliatum* have the potential to act as cheap feedstock [1-85, 110,111]. These sources play an ideal role in dealing with food insecurity [1-85, 110, 111-113]. Indigenous non-edible feedstock has been figured out as significant re-compensated to mitigate air pollutants and probably stop the food supply controversy debate [1-85, 110, 111-113].

Industrial hemp, a variant of the *Cannabis sativa* plant (*Cannabis sativa Linn*), is an important industrial and nutritional crop [65-109]. Hemp seed oil can be used to produce biodiesel though the process of transesterification [65-109, 110, 111-113]. Oil from hemp seeds presents a viable feedstock option for biodiesel production [70-113]. Another important advantage is that biodiesel requires no modifications to the diesel engine[1-109]. Hemp biodiesel presents a carbon neutral replacement to diesel fuel [70-109]. The carbon dioxide emissions released to the atmosphere when burning biodiesel is reabsorbed through photosynthesis [76-113].

The use of macro or microalgae as raw material for biodiesel production gives a solution to the treatment of a waste collected in the beaches [1-85]. In the algae biodiesel production process, it is necessary to extract the oil by crushing followed by solvent extraction [8-113]. However, the use of solvent for extraction may involved expensive separation process [8-113]. Recently, different authors have reported the biodiesel production via direct transesterification of raw oleaginous materials [8-113]. Direct transesterification can be carried out using homogeneous (acid or base) catalysts [8-113]. An alternative to direct transesterification is the microwave-assisted reaction [8-113]. The transesterification using microwave irradiation reduces significantly the reaction time. Moreover, the reaction time depends on the type of raw material both microwave and traditional transesterification [8-113]. One of the research work concluded that the best process conditions for microwave-assisted transesterification reaction are: macroalgae to methanol ratio of 1:15 (wt/vol), NaOH concentration of 2 wt % and the reaction time of 3 min [8-11].

Biodiesel, which is a mixture of fatty acid methyl esters (FAME), can be obtained by four methods: transesterification, pyrolysis, microemulsions, direct use and blending of raw oils [8-85, 110, 111-113]. Direct use is not suitable due to the high viscosity and low volatility of vegetable oils and animal fats [8-85, 110, 111-113]. Pyrolysis is defined as the cleavage to smaller molecules by thermal energy of vegetable oils over catalysts has been investigated [8-11]. However, it is a complicated process and produce side products without commercial value [8-85, 110-113]. Microemulsions with alcohols have been prepared to overcome the problem of high viscosity of vegetable oils. The most commonly used method is transesterification reaction in presence of a catalyst [8-113]. Transesterification is the reaction of an oil with an alcohol to obtain esters and glycerol [8-85, 110-113]. This reaction can be carried out in absence or presence of a catalyst [8-85, 110-113]. It is a reversible reaction [8-85, 110-113]. Therefore, it is necessary to use an excess of alcohol to shift the equilibrium to the product side [8-85-113]. The reaction occurs in three steps: (1) the conversion of triglycerides to diglycerides; (2) the conversion of higher glycerides to lower glycerides; (3) the conversion to glycerol [8-85, 110, 111-113].

The potential feedstocks for biodiesel production are edible (first generation feedstocks) and non-edible vegetable oils (second generation feedstocks), wasted oils and animal fats [1-85, 110-113]. First-generation biofuels are directly related to a biomass that is generally edible, and are usually produced from edible oils, such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut [1-85, 110-113]. Second-generation biofuels are fuels that are produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks to municipal solid wastes [1-85,110-113]. Third-generation bio-fuels are related to algae which have been considered as emerging non-edible oil sources of growing interest because of their high oil content and rapid biomass production, but could also to a certain extent be linked to utilization of CO_2 as feedstock [1-85, 110, 111-113]. However, the first generation bio-fuels seems to create some skepticism to scientists [1-85, 110, 111-113]. There are concerns about environmental impacts and carbon balances, which sets limits in the increasing production of biofuels of first generation [1-85, 110, 111-113]. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels [1-85, 110, 111-113]. Therefore, non-edible biodiesels feedstocks get great attention to overcome the problem that occurs due to continuous utilization of edible oils for biodiesel [1-85,110, 111-113].

3. Transesterification Reaction

In the transesterification reaction, in the first step, triglyceride reacts with methanol to produce diglyceride [1-113]. Furthermore, diglyceride reacts with methanol to produce monoglyceride [1-113]. Finally, monoglyceride reacts with methanol to produce methyl ester and glycerol[1-85]. By assuming that the reaction is a single step transesterification, the intermediate reactions of diglyceride and monoglyceride could be ignored [1-113]. Thus, stoichiometrically, the transesterification reaction required 3 mol of methanol and 1 mol of triglycerides [1-113]. Biodiesel can be produced by conventional transesterification method, i.e. homogeneous, heterogeneous, enzyme and advanced technology processes (microwave, ultrasound, or plasma assisted process) [1-85-113]. Plasma-assisted technology has several advantages compared with a conventional method, such as: shorter reaction time, no soap product, no glycerol product, and higher biodiesel yield [1-113].

Furthermore, plasma technology is very fast and rapid as compared to the existing conventional technologies [8-85]. There is a significant difference between heating with plasma technology and heating with conventional technology [1-113]. In conventional heating, the required reaction temperature is quite high, whereas in plasma heating, the required temperature is quite low but can produce high energy electrons with a temperature of about 10^4 K, so that it is able to excite the components in the reactants [1-113]. This is much different from conventional heating which has low energy in breaking bonds in the reactants[1-113]. Heating with plasma can significantly reduce the activation energy so that the reaction time can take place faster [1-113]. Yield of biodiesel produced over the plasma-assisted transesterification was higher significantly than the transesterification without plasma [1-113]. Meanwhile, the reaction time required or space time over the continuous flow hybrid catalytic-plasma reactor is very short compared to the conventional reactor [1-113].

The most common method for biodiesel production is transesterification, in which lipid and low carbon alcohol are commonly used as raw materials, in the presence of a catalyst [1-85, 110-113]. In the process of transesterification, the performance of the catalyst is the key factor of the biodiesel yield [1-85, 110-113]. The transesterification reaction involves the replacement of the alkyl group of an ester by another through interaction of the ester and alcohol [8-11]. Generally, this reaction is catalyzed by a base or an acid catalyst [8-11]. The basic catalysts are the most common since the process is faster and the reaction conditions are moderated [8-85, 110-113]. The first step is a catalytic reaction with alcohol, producing an alkoxide [8-85, 110-113]. The nucleophilic attack of the alkoxide to the carbonyl group of the triglyceride generates a tetrahedral intermediate compound from which the alkyl ester is formed [8-85, 110-113]. Finally, the catalyst is deionized, resulting in the regeneration of the active compound, which allows that it can react with a new molecule of alcohol, beginning a new catalytic cycle [8-85, 110-113]. Biodiesel is non-toxic, biodegradable and a portable fuel produced from renewable sources and it is one of the technically and economically feasible options to tackle the fast depletion of fossil fuels and environmental pollution [1-85, 110-113]. The other benefit of biodiesel fuel is that it can be used in any mixture with petro diesel fuel, as it has very similar characteristics [1-85, 110-113].

4. Biodiesel Production: Role of Catalysts

Catalyst is defined as a substance which increases the rate of chemical reaction without itself undergoing any permanent chemical change. Catalysts are not consumed by the chemical reaction and remain unchanged. The recent increase in the world biofuels demand, along with the need to reduce costs while improving the environmental sustainability of the biodiesel production are some of the major issues[1-113]. This has led to the search for catalysts that should be economically viable, efficient, and environmentally friendly [1-40]. Several classes of tin-based compounds ($SnCl_2$ catalyst, Sn(II)(3-hydroxy- 2-methyl-4-pyrone)2$(H_2O)_2$] complex catalyst, organometallic catalysts of Sn(IV) are potential catalysts for biodiesel production from transesterification reactions [1-85]. Catalysts used in biodiesel production are classified as homogeneous catalysts, heterogeneous catalysts, and enzymatic catalysts [1-113]. The incorporation of a catalysis-based transesterification reaction generally increases the rate of reaction and enhances the yield of the product [1-85-113]. There are various categories related to catalytic methods that provide an easy, efficient, and specific pathway for biodiesel production [1-113]. The component of biodiesel obtained by transesterification is close to that of traditional diesel[110-113]. It is widely used for its advantages of mild reaction conditions and less by-products than in the preparation of biodiesel [1-85]. In the process of transesterification, the efficiency is mainly affected by several factors including the quality of feedstock, the type of reactions, and the performance of the catalyst is the key factor of the biodiesel yield [1-85-113]. Readily available and inexpensive earth-abundant alkali metal species are used as efficient catalysts for the transesterification of aryl or heteroaryl esters with phenols which is a challenging and underdeveloped transformation [41-113].

Biodiesel is produced from vegetable oil or animal fat reacts in the presence of a catalyst (usually a base) with an alcohol (usually methanol) to give the corresponding alkyl esters (for methanol, fatty acid methyl esters). The use of microbial biomasses, such as fungal biomass, to catalyze the transesterification of triglycerides (TG) for biodiesel production provides a sustainable, economical alternative while still having the main advantages of expensive immobilized enzymes [42-85]. The use of fungal biomass cultivated on the microalgae recovered from wastewater treatment for the catalysis of transesterification reaction provides an additional piece of the puzzle of biorefinery[1-85-113]. Optimizing the transesterification reaction led to a valid prediction model with a final FAME concentration of 95.53%, w/w [42-113]. Biomasses of *Aspergillus flavus* and *Rhizopus stolonifera* were used to catalyze the transesterification of triglycerides (TG) in waste frying oil (WFO) [42-85]. Biocatalysts provide an eco-friendly option that usually catalyze the transesterification reaction under mild operation conditions and facilitated product separation without any byproduct formation [42-113]. Employing enzymes for the catalysis transesterification reactions face critical problems, such as the cost and stability of enzymes [42]. The use of microbial biomasses to catalyze transesterification, such as fungal biomasses, has been gaining research interest [42-113]. The main advantages of immobilized enzymes is that reusability, mild reaction conditions, the capability of catalyzing glycerides and free fatty acids (FFA), no risk of saponification, producing high degree glycerol as a side reaction, short reaction time, and being an environmentally friendly option [1-42]. Microalgae bio-refineries could efficiently fulfill a considerable part of the increasing fuel demand and reduce greenhouse gases, directly interacting with global warming and climate change [42-113].

The transesterification process can be directed through a homogeneous mode or heterogenous mode [1-85]. The homogeneous catalysis process is initiated through faster reactions and lower loading processes when compared to the heterogenous mode of production [1-113]. The major disadvantage of using the homogeneous mode of biodiesel production is related to the inefficiency in reusing it, thus providing a non-economical medium of production [1-12-42]. The heterogeneous catalysis process has the ability of converting the biodiesel with significantly lower amounts of fatty acids and water composition, thus providing higher selectivity, activity, and water adaptability due to the availability of various active sites [1-85]. Homogeneous catalysts function in the same phase (whether they are in liquid or gaseous form) as the reactants [1-12]. Ideally, the homogeneous catalyst is dissolved in a solvent along with the substrate, which can be either an acid or a base [1-113]. Homogeneous acid and base catalysts such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), sodium hydroxide (NaOH), and potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$) are the most common homogeneous catalysts used in transesterification reactions [1-113]. In industrial-scale biodiesel production, the most common homogeneous base catalysts are usually KOH and NaOH [12-85]. They have been shown to have high catalytic activity and are traditionally used commercially as low-cost catalysts [12-85]. Furthermore, homogeneous base catalysts are the most viable catalysts for mass production because the transesterification process using base catalysts is performed under low pressure and temperature conditions, conversion rate is faster in a short period of time, the conversion rate is outstanding with no intermediate steps, and the process is cost effective [1-12-85-113]. In fact, it was reported that the rate for a base-catalyzed reaction would be 4000 times faster compared to an acidic catalyst [1-12].

Therefore, homogeneous catalysts are currently the most widely used catalysts in industry [1-12]. Homogeneous catalysts have the characteristics of uniform active centers and fast reaction rates [12-40]. It can be seen that homogeneous catalysts cannot be reused or regenerated, which is one of their major disadvantages [12-85]. The separation of a homogeneous catalyst from products is difficult [1-12]. Homogeneous catalysts are partially miscible in biodiesel and miscible in glycerol, which results in problems of product separation from the reactant mixture [1-12-85]. This requires more equipment to separate and results in a higher production cost [1-12]. In addition, the biodiesel yield of homogeneous acid catalysts will be a little higher compared to homogeneous base catalysts, but the homogeneous acid catalysts have problems such as the necessity for washing the products for catalyst removal and equipment corrosion [1-12-85]. The poor yield of biodiesel prepared by homogeneous base catalysts is due to problems such as saponification [1-12]. Excessive soap in the products can drastically reduce the FAME yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing [1-12-85-113]. However, homogeneous base catalyst reactions are highly sensitive to the presence of FFAs and water [1-12]. The homogeneous base catalysts are extremely hygroscopic and able to absorb water from the air throughout storage [1-12]. The homogeneous base catalysts also produce water when dissolved in the alcohol reactant and thus affect the yield [12-85]. In addition, the soap solution from the neutralization and saponification side reactions can hinder the separation and purification processes and generate large amounts of wastewater, and increasing costs [1-85-113]. Currently, the most of the catalysts used in biodiesel industrial production are homogeneous catalysts, but these catalysts are not applicable to all types of feedstocks [12-85]. Moreover, homogeneous catalysts have the problem of not being reused or regenerated, which greatly increases the cost of biodiesel production [12-85]. Homogeneous catalysts suffer from difficulties in separation [12]. Heterogeneous solid catalysts are simple to separate, but still fall short of the expected goals for industrial use, and the residual catalyst has a large impact on biodiesel quality [12]. In addition, homogeneous alkaline catalysts are corrosive and are non-recyclable, that comprises the main disadvantags of its use in the biodiesel production [12].

Acid catalysts have a better tolerance level in processing waste oils for biodiesel production than base catalysts [12-113]. In two-step transesterification processes, acid is preferred as a catalyst first followed by a base for better results, especially when using organic substrates [12-113]. Homogeneous acid catalysts can be used to synthesize biodiesel from renewable feedstocks such as animal fat, grease, and waste cooking oil [12-113]. In addition to slow reaction times, homogeneous acid catalysts are corrosive, lead to excessive amounts of wastewater, and complex procedures are required to separate the catalyst from the reaction products for reuse [12-113]. This has led to the development of heterogeneous acid catalysts for this process. In recent years, a new type of homogeneous catalyst, ILs/DESs, has been derived based on the traditional homogeneous catalyst[12-113]. ILs are new green solvents composed of inorganic or organic anions and organic cations, usually as salts in the molten state [12]. The use of IL as a catalyst, a co-solvent, or an extracting solvent has recently attracted attention in the field of biodiesel production [12-85]. The applications of the homogeneous and heterogeneous catalyst derivatives ionic liquids (ILs)/deep eutectic solvents (DESs) and nanocatalysts/magnetic catalysts in biodiesel production are reviewed[1-85-113]. In recent years, DES catalysts have also started to be used in biodiesel production [12-113]. Ranjan et al., 2022 [12, 13-15] used crude glycerol–choline chloride-based deep eutectic solvents (DES) and NaOH as catalysts for the preparation of biodiesel, using waste cooking oil as the raw material [13-85]. The results showed that the biodiesel yield was up to 95% at the optimum reaction temperature of 65^{o} C and reaction time of 90 min [12, 13-15].

Heterogeneous catalysts (CaO, SO_4/Fe-Al-TiO_2, MgO, Fe-Mn-SO_4/ZrO_2, O_3/ZrO_2, aO/$CuFe_2O_4$) generally more suitable for continuous biodiesel reaction processes [1-12]. Adsorption is an important step in the transesterification reaction by heterogeneous catalysts [12-85-113]. Compared with homogeneous-type catalytic transesterification and esterification, heterogeneous catalysts are widely studied due to their high activity, high selectivity, easy separation from the products, and reusability [12-17-85-113]. Several types of solid base catalysts have been utilized for biodiesel production, such as base metal oxide, base metal carbonates or hydro-carbonates, anionic resins, and basic zeolites[1-12-85-113]. It can be seen that heterogeneously catalyzed transesterification generally requires more severe operating conditions (relatively elevated temperatures, pressures and higher alcohol-to-oil molar ratio), and the performance of the conventional heterogeneous catalysts is generally lower compared to homogeneously catalyzed transesterification [1-12-85-113]. Moreover, the separation and subsequent purification of the reaction products are relatively simple, and the recoverability of the catalysts is improved because the heterogeneous catalysts do not required water washing in the production of biodiesel, which simplifies the purification of the products [12-85]. However, the heterogeneous catalysts suffer from catalyst poisoning and leaching [12-85]. The poisoning problem is particularly pronounced when the catalytic process involves used cooking oils [12-113]. The more serious problem is catalyst leaching, which increases the operational cost due to the need for catalyst replacement and leads to product contamination [12-85-113]. Heterogeneous acid catalysis has a lesser toxic effect and gives rise to fewer environmental problems compared to the homogeneous mode [12-85-113]. Several heterogeneous base catalysts, such as base earth metal oxides, base-doped alumina, hydrotalcite, and base zeolites, have been widely used for biodiesel preparation[12-85]. Both homogeneous and multiphase catalysts have their own unique advantages for biodiesel production, but both also have drawbacks that hinder their large-scale industrial application [12-85]. Heterogeneous catalysts are widely studied due to their high activity, high selectivity, easy separation from the products, and reusability [12-85]. Compared with conventional heterogeneous acid catalysts, HPA heterogeneous catalysts have better catalytic performance[12-85-113].

5. Conclusion

Energy demand is expected to increase due to rapid population growth, expanding urbanization and better living standards. Fossil fuels remain the dominant source of energy though it is non-renewable and has negative impact on global climate. Biodiesel is more expensive to produce and has a slightly lower energy content compared to fossil fuels. The high cost of production will reduce the market value and use. Technology, catalyst, and feedstock costs are key in determining the cost of biodiesel production. The cost of each specific catalyst depends on various factors, including the source, synthesis method, and its reusability. Generally, using waste or biomass as sources of catalysts may reduce the price of commercially available solid catalysts. Thus, the preparation of heterogeneous catalysts for biodiesel from biomass or waste is an economical and environmentally feasible method. Short catalyst lifetime, low reaction rate, and high fabrication cost are the main problems of heterogeneous catalysts. In case of homogeneous catalysts, there are problems of catalyst poisoning and contamination. In addition, active site leaching and saponification problems can lead to significant contamination generation. Development of efficient biomass-derived catalysts for biodiesel production to reduce the associated costs is warranted. The introduction of HPA heterogeneous catalysts and nanocatalysts with excellent catalytic properties has improved the reaction efficiency and increased the service life of the catalysts. Homogeneous and heterogeneous catalysts are the most researched biodiesel catalysts. Homogeneous catalyst derivatives ILs/DESs possessed excellent properties of both homogeneous and heterogeneous catalysts with higher stability and reusability. Several classes of tin-based compounds are potential catalysts for biodiesel production from esterification or transesterification reactions.

Compliance with ethical standards

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