J Ther Eng, Vol. 10, No. 5, pp. 1362–1389, September, 2024

Journal of Thermal Engineering
Web page info: https://jten.yildiz.edu.tr
DOI: 10.14744/thermal.0000826

Review Article

Biodiesel production from waste cooking oil: A review on production methods, recycling models, materials and catalysts

Atefeh AHMADBEIGI[1], **Mahdi MAHMOUDI**[2], **Leila FEREIDOONI**[2], **Mojtaba AKBARI**[2], **Alibakhsh KASAEIAN**[2,*]

[1]*School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, 14155-6619, Iran*
[2]*College of Interdisciplinary Science and Technology, University of Tehran, Tehran, 14155-6619, Iran*

ARTICLE INFO

Article history
Received: 26 May 2023
Accepted: 16 February 2024

Keywords:
Biodiesel; Intensification Techniques; Recycling Model; Renewable Energy; Thermal Process

ABSTRACT

The imperative for sustainable energy development has become increasingly evident, primarily due to the finite nature of fossil fuel reserves and the associated environmental apprehensions. In light of these concerns, biodiesel emerges as a compelling alternative. Its key attributes include renewability, reduced emissions, and the ability to be produced from a variety of sources, rendering it a promising candidate in addressing these energy and environmental challenges. Biodiesel holds significant promise as an energy source due to its lower environmental impact compared to traditional diesel fuels. This alternative fuel is non-toxic, safe, and biodegradable, primarily derived from renewable biological feedstocks like used cooking oils, making it an affordable and sustainable resource. This paper provides a comprehensive review encompassing biodiesel properties, feedstock options, diverse production techniques, catalyst variations, and the challenges associated with biodiesel production. Furthermore, this study delves into the evolution of biodiesel conversion processes and innovative approaches to enhance scalability. Detailed examinations of pivotal factors influencing transesterification, including catalyst weight percentage, temperature, alcohol-to-oil molar ratio, and reaction duration, are presented. Ultimately, this review concludes with future perspectives and suggestions. It emphasizes the importance of judiciously selecting catalysts, feedstock materials, and production methodologies to develop cost-effective, energy-efficient biodiesel solutions with reduced environmental impact and enhanced operational efficiency.

Cite this article as: Ahmadbeigi A, Mahmoudi M, Fereidooni L, Akbari M, Kasaeian A. Biodiesel production from waste cooking oil: A review on production methods, recycling models, materials and catalysts. J Ther Eng 2024;10(5):1362–1389.

INTRODUCTION

Recently, many research studies have been devoted to alternative fuels due to the increase in oil prices and environmental pollution concerns regarding the combustion of fossil fuels [1]. Nowadays, the worldwide growing need for new energy resources, particularly for the transportation, is one of the main challenges of countries [2].

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*Corresponding author.
*E-mail address: akasa@ut.ac.ir

This paper was recommended for publication in revised form by Editor-in-Chief Ahmet Selim Dalkılıç

Published by Yıldız Technical University Press, İstanbul, Turkey

the current fossil fuel resources are not sufficient for future global demand because they are limited and have increased concerns about environmental issues such as greenhouse gases (e.g. carbon monoxide, nitrogen, and sulfur) [3]. Other problems are the limited refining capacity in the world and the pollution caused by fossil fuels and their fineness [4]. Considering global warming and climate change, renewable sources of energy play a key role, as they are sustainable and reduce greenhouse gas emission [5].

Recent years have seen dwindling resources, increased energy demands, and severe environmental impacts drive the research into alternative energy [6]. The developed countries have started to take action for the future energy crisis by developing considerable measures and goals, but the energy demand is still increasing with the population growth. It is expected that developing countries such as India, China, and Brazil consume higher energy due to the growth of their population and economy, and the estimated global oil consumption will reach 17 million BTe (Billion-ton equivalent) by 2030 [7]. Consequently, the growth of the population and the subsequent increase in energy demand contribute to the continuous increase in energy demand. In addition, the degradation of the environment caused by the use of fossil fuels and the associated consequences appear to be an unbearable concern. It is therefore essential that researchers shift to renewable energy sources, not only due to resource depletion but also in order to avoid the consequences of an unclean environment and relevant adversities produced by fossil fuels [8]. Despite the considerable growth in renewable energy usage, it has not even reached half of the global energy demand yet. Intensive research studies in recent decades on developing efficient alternatives to conventional fuels have resulted in some scientific approaches [9]. Biofuels have been specifically identified as a superior alternative fuel to fossil fuels among a wide range of alternative fuels because they are extracted or produced from biological sources such as lipids of animal fat, oleaginous plants or microbes, and municipal organic wastes [10]. Also, lignocellulosic substances and wastes have been considered as cheap sources for biofuel and bioethanol production [11]. Some of the biofuels are biogas, crude bio-oils, biodiesels, bioethanol, and biohydrogen, among which liquid fuels are greatly attractive for direct use in conventional engines [12]. The research on liquid fuels is vital because about 90% of engines are powered by diesel and gasoline [13]. Biodiesel would be an excellent alternative or additive for fossil fuels [14]. Thus, biodiesel can satisfy the requirements for an environmentally friendly, renewable, and efficient liquid fuel as a promising alternative to fossil diesel without the need for considerable engine system modification [15].

Vegetable oil was first used in the combustion engine by Rudolf Diesel in 1893. Despite the low-price and abundance of the oil, refined crude oil was used as diesel fuel in diesel engines [16], because the direct use of such oils in diesel engines faced many problems due to the large size of triglyceride molecules and their high viscosity and molecular weight. These drawbacks can be eliminated by modifying the chemical structure of animal and vegetable oils. In fact, the reaction between alcohol and oil results in biodiesel, which consists of monoalkyl esters mixtures of long-chain fatty acids. Biodiesel can be considered as a carbon-free fuel without any release of carbon monoxide, unburned hydrocarbons, and particulate matters, in particular sulfur, in comparison with the conventional diesel. It has also shown that biodiesel emit less pollutants and greenhouse gases in comparison with petro-diesel. Biodiesel can reduce the CO_2 emissions up to 78% compared to petro-diesel owing to the closed carbon cycle in biodiesel [17]. The carbon cycle is the process, in which, the emitted carbon molecules to the atmosphere are absorbed by the Earth's natural processes [18]. According to Figure 1, biodiesel does not emit

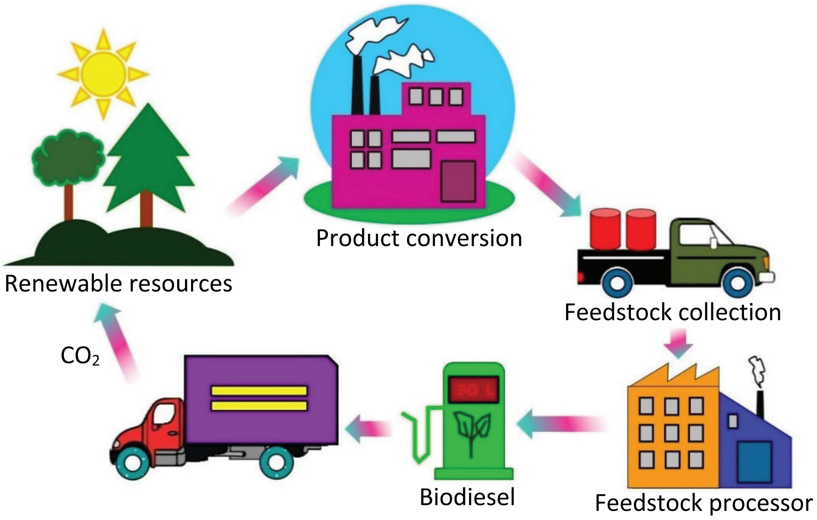


Figure 1. Schematic representation of carbon cycle in biodiesel production.

pure carbon; instead, the whole carbon dioxide, produced by biodiesel burning, is absorbed by the plants which are the source of biofuel [19, 20].

Biodiesel, compared to conventional diesel fuel, presents unique properties that are crucial for its application in various engine technologies [21]. One notable aspect is its potential to increase NO_x emissions in engines with certain fuel systems, attributed to its compressibility [22]. The reasons behind this effect in common rail engines require further research. However, strategies like cetane improvers, adjusting biodiesel composition, and injection timing can mitigate these NO_x effects [23]. Biodiesel also reduces soot formation in diesel flames, leading to decreased particulate emissions. While it might not be the most effective soot suppressant, it alters the characteristics of the soot produced during combustion, making it more reactive to oxidation. The precise mechanisms driving these changes warrant further investigation [24, 25].

This review paper comprehensively investigates innovative methods for the production of biodiesel from waste cooking oil. In addition to dealing with biodiesels, this paper also explores sustainable energy sources in order to decrease the production costs by utilizing more effective catalysts and raw materials such as waste cooking oil. The challenges related to the production of biodiesel and scalability are also investigated in this paper. It has been shown in this paper that proper selection of the catalyst, raw materials, and the synthesis method significantly determine the cost-effectiveness, energy efficiency, and environmental effects of the produced biodiesels. Recent advances in the field of production of efficient and sustainable biodiesels, known as 'Biodiesel Production by Electrolysis', have been also addressed in this review paper. In addition, different recycling methods are discussed to efficiently reuse waste cooking oil as a promising energy source, thereby alleviating the environmental issues of this waste material.

PHYSICAL AND CHEMICAL PROPERTIES OF BIODIESEL

Different countries have set standards and policies for the production and continuous utilization of high-quality biodiesel as part of their energy mix [26]. Table 1 lists the required properties of methyl esters as biodiesel according to EN14214 (EU) and ASTM D6751 (USA) standards. these parameters significantly affect the fuel injection in diesel engines and are necessary to avoid undesirable effects on

Table 1. Biodiesel properties specified in EN14214 (EU) and ASTM D6751 (USA) standards

Property	Unit	ASTM D6751 (USA)		EN14214 (EU)	
		Test Method	**Limits**	**Test Method**	**Limits**
Cetane number (CN)	-	D 613	Min 47	EN ISO 5165	Min 51
Acid value	mg_{KOH}/g	D 664	Max 0.50	EN 14104	Max 0.50
Density (15°C)	kg/m^3	ASTM D 1298	Max 880	EN ISO 3675, EN ISO 12185	Max 900
Kinematic viscosity (40°C)	mm^2/s	D 445	Max 6.0	EN ISO 3104, ISO 3105	Max 5.0
Flash point	°C	D 93	Min 130	EN ISO 3679	Min 120
Sulfated ash content	(m/m) %	D 874	Max 0.02	ISO 3987	Max 0.02
Cloud point	°C	D 2500	−3 to −12	EN 116	Max −4/3
Amount of water	mg/kg	D 2709	Max 0.05 (v/v %)	EN ISO 12,937	Max 500
Sulfur content	mg/kg	D 5453	Max 0.05 (m/m %)	EN ISO 20846, EN ISO 20884	Max 10.0
Carbon residue	(m/m) %	D 4530	Max 0.05 (100% sample)	EN ISO 10370	Max 0.30 (10% sample)
Iodine value	g I/100 g	-	-	EN 14111	Max 120
Phosphorus content	mg/kg	D 4951	Max 0.001 (% m/m)	EN 14107	Max 10.0
Ester content	(m/m) %	-	-	EN 14103	Min 96.5
Methanol content	(m/m) %	EN 14110	Max 0.20	EN 14110	Max 0.20
Copper strip corrosion (3hrs, 50°C)	class	D 130	Max No. 3	EN ISO 2160	Max No. 1
Total glycerine	(m/m) %	D 6584	Max 0.240	EN 14105	Max 0.25
Alkali metals (Na + K)	mg/kg	EN 14538	Max 5.0 ppm (µg/g)	EN 14108, EN 14109	Max 5.0
Earth alkali metals (Ca + Mg)	mg/kg	EN 14538	Max 5.0 ppm (µg/g)	EN 14538	Max 5.0

the fuel injector performance [27]. ASTM standards have specified the maximum density (which can be calculated according to EN/ISO 3675 or ASTM D 1298 test methods) and viscosity of 880 kg/m^3 and 6.0 mm^2/s (which is nearly similar to that for diesel fuel) for biodiesel, respectively. The carbon residue value in all standards is approximately the same [28]. The acid value can be measured by the methods described in EN 14104 or ASTM D664 standards.

Resources for Biodiesel Production

Low production cost and the ability of large-scale production are among the most important factors which affect the selection of raw materials for biodiesel production [29]. Some of the main factors, affecting the availability of raw materials for biodiesel production, are geographical location, agricultural practices, regional climate, and local soil conditions in each country. Raw materials account for about 80% of the biodiesel production cost [30]. Raw materials are mainly selected based on their price and availability [31]. Biodiesel can be produced using more than 350 types of oil products as potential raw materials [32]. There are numerous types of raw materials for biodiesel production including but not limited to waste cooking oil (WCO) [33], vegetable oils [34], animal fats [35], algal oil [36], jatropha oil [37], waste grease [38], microbial oil [39], tallow [40]. The non-edible oilseeds (such as castor, linseed, cottonseed, cuphea, bahapilu, karanja, jatropha curcus, nagchampa, mahua, neem, tonkabean, and rubberseed) and edible oilseeds (such as cardon, ethiopian mustard, gold-of-pleasure, and tigernut) could be considered as the inexpensive oil sources [41]. Vegetable oils have numerous advantages. Firstly, they can be found almost in every country. Secondly, they are renewable because they can be planted and harvested several times during the year. Thirdly, they can potentially produce green fuels because they do not have any trace elements, especially sulfur. Lastly, plants contribute to stabilizing carbon dioxide via photosynthesis [42]. As the main drawbacks, vegetable oils have a higher viscosity than biodiesel. A plant growth also requires large amounts of chemical fertilizers, leaving trace amounts of carbon due to the increased demand for biodiesel raw material leading to a kind of increase. In addition, some food items are expensive [43]. Thus, it is of high importance to find inexpensive raw materials with less limitations for biodiesel production so as not to diminish food resources [44].

In recent years, microalgae have attracted the attention of researchers due to their special properties as a promising source for the production of biodiesel [45]. They can produce large amounts of oil; the oil production efficiency of some microalgae reaches 70% of their dry weight. Microalgae can adapt themselves to diverse environments and conditions. They can even consume sewage and contaminants and can be irrigated by seawater. They are also capable of storing different substances (e.g. fat) in their tissues based on the environmental conditions and the nutrients they receive. These features have attracted the attention of researchers to the microalgae. The production of biodiesel from algae oil is the same as the conversion of vegetable oils to biodiesel [46].

The production of biodiesel from waste edible oils is a promising approach since they have much less cost than fresh oils [2]. In addition to the reduction of biodiesel cost, it is possible to recover and reuse wastes by using low-cost waste edible oils and animal fats instead of refined edible oils [47, 48]. Among all types of raw materials for biodiesel production, WCO has gained significant attention due to its beneficial properties such as its abundance, sustainability, reduced environmental impact, cost-effectiveness and so on [49]. WCO is a residual oil collected after cooking and consists of free fatty acids (FFA), making it a technically promising raw material for biofuel production [50]. It is inexpensive and widely available from food processing industries, restaurants, fast food outlets, and households. In addition, using WCO, as a worldwide sustainable alternative for biofuels production, can balance oil resources and edible oil-based food products [51]. Cooking oils are mostly produced from edible oil plants and may be used several times for frying due to economic reasons, which cause the reaction of dissolved oxygen in the oil with unsaturated acylglycerols. This case could result in the formation of various compounds such as polyglycerols, dimeric acylglycerols, and dimeric and polymeric acids. At last, these compounds can cause the cooking oil to become more viscous [41]. Further use of WCO is harmful to human health, because lipid burning increases the oil's acidity and unpleasant odor. Additionally, the WCO has high amounts of water and free fatty acid; so, it has a low economic value as a source for efficient biofuel conversion [52].

The stored oil after being cooked, which contains free fatty acids, could be a suitable raw material for converting into biofuels [50]. As a result of its extensive resources from restaurants, fast food outlets, food processing industries, and households, it is also very accessible, affordable, and widespread. Also, because WCOs are produced worldwide, they can provide a viable alternative to biofuels by reducing the competition between oil resources and edible oil-based foods. Continuous use of oil for frying causes oxygen to dissolve in the oil to react with acyl unsaturated glycerols [41]. Reusing WCO is harmful for human consumption because browning causes the oil to become acidic and emit an unpleasant odor. Therefore, due to the high content of free fatty acids, water, and gross solids in cooking oil, that has been used several times, and its low economic value, its disposal in the environment could result in many problems [52].

The disposal of WCO is becoming a global issue [53]. These issues have led to the creation of regulations governing WCO disposal and recycling, as well as encouraging researchers to develop innovative approaches to producing value-added products. Recycling WCO has attracted the attention as a promising approach for biofuel production [54].

The collection and recycling models, obtained from different local policies, could be applied to make use of WCO as a fuel source. In addition to the economic benefits of using WCO, as a raw material for biofuels production, the public health problems and environmental hazards, caused by WCO disposal, are also eliminated. It should be noted that the handling and recycling of WCO depends on the countries in question [53, 55]. The next section discusses some models for the collection and recycling of WCO that have been used in some WCO-producing countries, such as the United States (USA), the European Union, Japan, and China.

A number of models have been suggested for collection and recycling of WCO, providing opportunities for the production of biofuels using this valuable raw material. In this way, in addition to the great economic benefits of biodiesel production from the WCO, the environmental risks and public health problems caused by the WCO discharge are also reduced.

More than half of the vegetable oils produced worldwide are consumed by the United States, China, India, and member countries of the European Union [56]. Some of the acts in the USA, for strict control of the waste recovery include the Pollution Prevention Act of 1990, Solid Waste Disposal Act (1960), and Energy Policy Act (2005). It has been reported that the subsidy of 0.50 USD/gallon for the production of biodiesels from recycled oil in the US has increased the WCO recycling rate to about 100%. The same model is used in Japan for WCO recycling. The stakeholders in this field are government, private waste oil collection companies, biodiesel companies, and restaurants. Restaurants have to pay the waste recycling companies for processing the wastes. The waste oil recycling companies have to pay the business fees set by the government. On the other hand, the biodiesel companies can receive subsidies and enjoy tax exemption. The Japanese and the USA models have considered high recycling rates for biodiesel enterprises due to reward mechanism and strict control [55]. The business model for WCO recycling in the US is depicted in Figure 2.

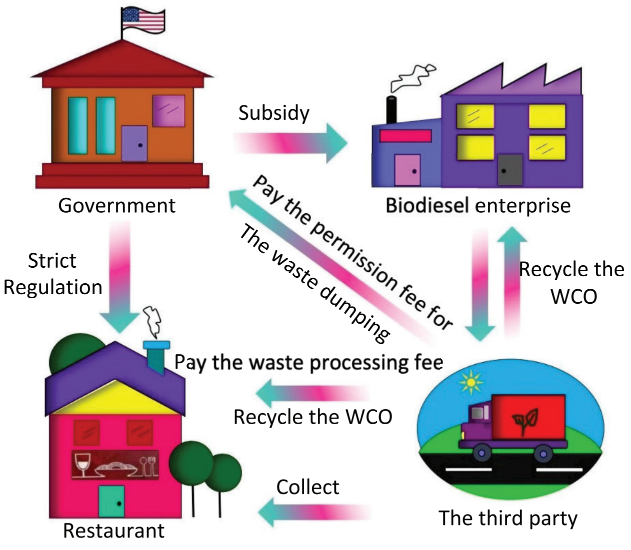


Figure 2. Business model for WCO recycling in the US.

The largest global biodiesel and the third biggest biofuel markets belong to Europe. Imposing income taxes and decreasing the dependency on importing crude oil are the two key factors for the development of this industry [57]. The total WCO, generated in the EU countries from 2016, is about 1,660,000 tons/yr from which 854,000 tons/year belongs to households, while 806,000 tons/yr are produced in professional industries with the recovery rate of 5.6% and 86%, respectively. The specified goal by the Renewable Energy Directive (RED) of the European Union in 2020 for the amount of renewable energy, consumed in the transportation sector (RES-T), was 10%. To this end, the first-generation biodiesel and the first-generation ethanol were mixed with conventional diesel and gasoline, respectively. In 2015, the risk of indirect land use change (ILUC), due to biofuel production, was minimized by a set of criteria for biofuel sustainability established by the RED. Accordingly, double-counting the energy of biofuels obtained from waste raw materials in RES-T share prompted increased biodiesel production share using WCO and residual fats to 25% in EU (i.e. 1.4% of the total energy consumption in transportation). Fuel providers are compelled (by fines across the EU) to satisfy the lowest amount of blending content in their end products, growing the demand for WCO. This issue led to an increase in the imports mainly from China and exceeding the WCO price from that of edible oils. A number of unofficial reports indicate that many of the WCO used as feedstock for biodiesel production in Europe is counterfeit and cannot be traced [53, 58]. To deal with this problem, the Directive (EU) 2018/2001 of the European Parliament as well as that of the Council of 11 December 2018 on the Promotion of the Use of Energy from Renewable Sources was established to trace the origin of WCO and set a maximum limit for biofuels produced from WCO (about 1.7% of energy required in transportation section without double-counting rules). As a result, the uptake was regulated based on the availability of WCO in EU and the production of advanced biofuels was promoted. These directives resulted in many implementation plans and initiatives in different countries such as Belgium and Austria, which were successful in collecting WCO throughout the country up to 0.73 and 1 kg per capita, respectively. Valorfrit, as an umbrella association in Belgium, coordinated the WCO collection throughout the country [53]. Oil sellers and distributors were obligated by the federal government to obey WCO recycling program in order to efficiently trace oil and WCO on the market via the centralized collection. As a result, almost 64% of the household WCO and nearly all WCO from the professional sectors were collected in Belgium (i.e. a collection efficiency of more than 80%) [59], 98% of which was used for biodiesel production. The pathway for such a traceable oil supply chain is illustrated in Figure 3.

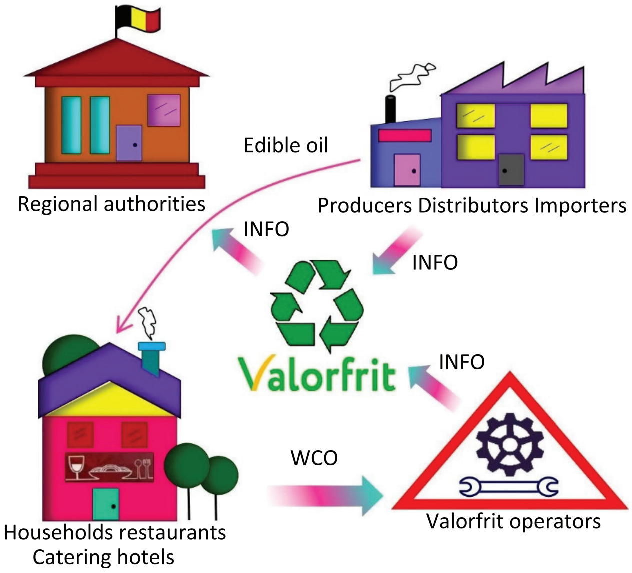


Figure 3. Traceable and centralized collection of WCO according to EU model performed in Belgium.

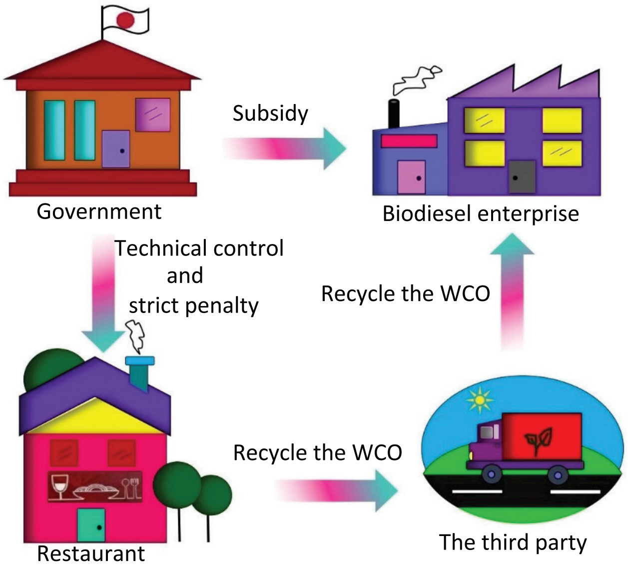


Figure 4. The Japanese business model for WCO recycling.

About 0.1 to 0.5 million tons/year WCO is produced in Japan [55, 56]. After 1997, many Japanese towns, including Yokaichi, Aito, Shinasahi, and Imazu, as well as local municipalities inside the Kagawa and Shiga regions started to convert WCO to biodiesel for their municipal vehicles instead of disposing it down the sewer [60]. Biofuel or licensed transportation enterprises can only use the WCO. In this recycling model, the biofuel production costs can be reduced by providing subsidies to the relevant enterprises, fortifying its price competitiveness with counterfeit products, and hence, further increasing the WCO recovery rate [53]. Consumers who entirely use biofuel instead of fossil fuels in their vehicles are exempted from transaction taxes [61]. Third-party take-back (TPT) is a commercially feasible model because it considers some developed recycling technologies and third-party recycler in the supply chain. However, it has been reported that there is a cost difference between the two parties. The Japanese government increased the WCO recycling rate by providing tax incentives and subsidies based on the Act of Food Waste Recycling in 2001 and the Promotion Law on Effective Utilization of Resources in 2000 [55]. In this recycling model, restaurants, biodiesel and transportation enterprises as well as the government are considered as stakeholders. Japanese utilized a device for separation of oil and water in their collection system to obtain pure WCO. Filters or separation systems were required in the restaurants to separate water from WCO and food wastes; thus, the waste draining in the sewer is avoided. In addition, subsidies were granted and severe technical regulation measures were implemented to the biodiesel enterprises by the Japanese government [53]. The Japanese business model for WCO recycling is shown in Figure 4.

It is estimated that about 5 million tons/year WCO is produced in China. The China government granted different subsidies to recyclers with the aim of encouraging the management and collection of WCO and avoiding its illegal recycling [61]. By encouraging and regulating the utilization of WCO for the production of clean power, especially biodiesel, the WCO disposal in restaurants has become financially practical [62]. By 2020, according to the China's 13th Five-year Economic and Social Development Plan (2016-2020), the investments in biomass energy, especially biofuels produced from inedible raw materials, would increase to 18 billion Chinese Yuan [63]. Generally, the WCO recycling modes in China can be considered either as the third-party take-back (TPT) or biodiesel enterprise take-back (BET). The first mode was applied in developed countries including Japan and the US where the WCO recycling and biodiesel production processes are considered separately; while the latter mode with some modifications was adopted in Chinese cities such as Ningbo and Suzhou [53, 64]. Some transportation and storage processes were integrated by the Suzhou government to avoid dependent recyclers. On the other hand, in Ningbo, the government provided centralized transportation and collection along with professional disposal, market-oriented collection system, public participation, and legal management. The Chinese government set up particular funding plans and carried out recovery experiments in thirty-three cities to support resource recovery and avoid harmful disposal of WCO. By these actions, the kitchen waste, produced in large restaurants and enterprises, could be collected and transported separately; whereas, smaller enterprises could transport their waste to the "urban environment and sanitation management" organization by paying the determined fees [53].

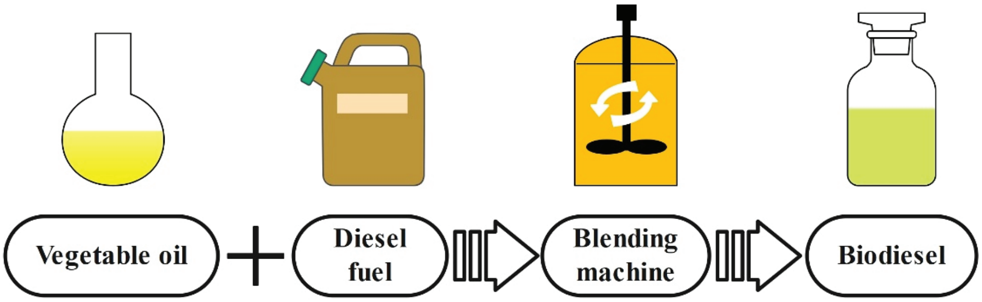


Figure 5. Schematic of blending (dilution) method for biodiesel production.

Biodiesel Production Methods

Blending or dilution method

It was originally intended that vegetable oils would be used directly as fuel for diesel engines. Peanut oil was first used successfully as a biomass fuel for diesel engines by the inventor of diesel engines, Rudolf Diesel [65]. Some of their advantages as fuel are their renewability, appropriate heat content, facile transportation, and abundance. On the other side, some of their disadvantages are high viscosity, defective combustion due to oil impurities, low flammability and volatility, presence of high chemical-activity unsaturated hydrocarbons, ring adhesion, and deposition of carbon zinc on engine parts [66]. The schematic of blending method for biodiesel production is illustrated in Figure 5.

Non-catalytic supercritical method

High conversion yield and reaction rates at very short times can be achieved via the non-catalytic supercritical transesterification method, in which, the separation and purification steps are performed more easily in the absence of catalyst. In this method, free fatty acids or water content of oils do not influence the biodiesel synthesis. In addition, it does not require pre-treatment processes for water removal from the oils. This method is usually performed at 10-25 MPa and 200-400°C. In other words, these parameters should be higher than the critical pressure (Pc) and temperature (Tc) of alcohol to obtain higher solubility in oils [67]. For example, in the case of methanol, the reaction pressure and temperature should be higher than 8.09 MPa and 239°C, and 8.09 MPa, respectively [68]. As a result, this process is energy consuming and needs high temperatures, which makes it economically inefficient for industrial applications. The lack of oxygen in the thermal cracking process also decreases the oxygen content in the final fuel [69]. Figure 6, presents the production of biodiesel via supercritical methanol process from WCO [70].

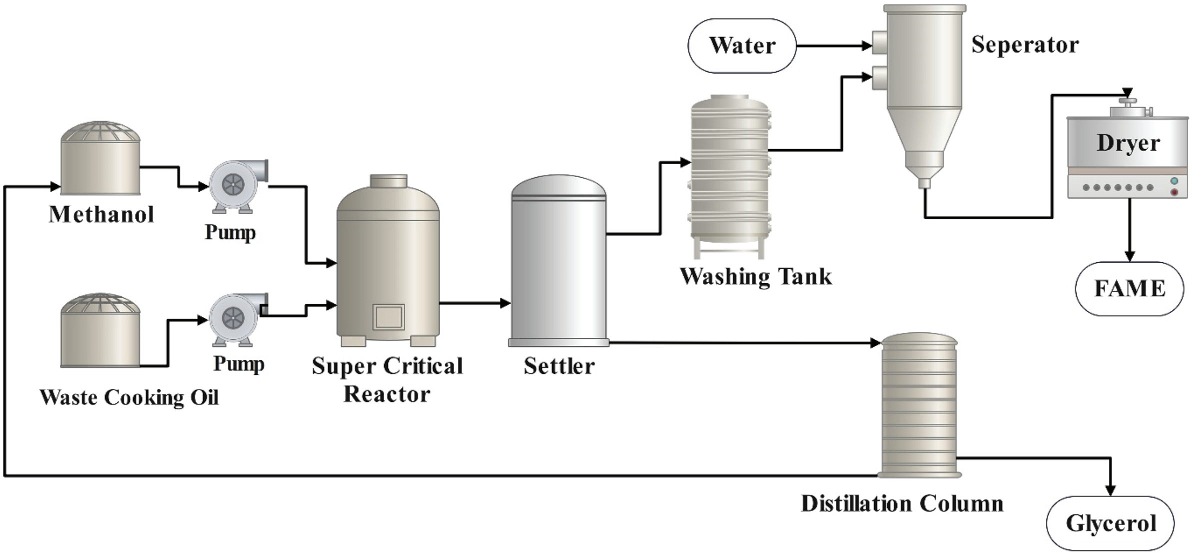


Figure 6. Schematic of biodiesel production from WCO by supercritical methanol process.

Microemulsification

Microemulsions, as colloidal dispersion, could be conducted by mixing of oil, water, and surfactant. They are transparent and thermodynamically stable with the capability of eliminating concerns about the viscosity of vegetable oil. The microemulsion droplets are in the range of 100 to 1000 Å. Oil microemulsions could be obtained by the addition of alcohol, surfactant, cetane improver, and co-solvent. Microemulsions, made by hexanol, butanol, and octanol can satisfy the required viscosity for fuel. Microemulsification is a straightforward method and has advantages such as stability, high viscosity and low volatility [71, 72]. Their nonionic and ionic characteristics are similar to those of diesel fuel. In short-term operation, they showed acceptable spraying behavior with improved combustion properties due to their explosive evaporation. In long-term operation, they also showed no considerable performance failure [73, 74]. Carbon deposition on the injector nozzle chocking and piston head as well as gum formation are some consequences of high viscosity [27]. An example of microemulsification method is to produce biodiesel fuel through the extraction of vegetable oil using diesel-based reverse-micellar microemulsions as a solvent. In this technique, peanut oil is extracted directly into the oil phase of the microemulsion based on the principle of “likes dissolve likes,” resulting in a blend of peanut oil and diesel [75].

Pyrolysis method

A substance can be converted to other products by heating, with or without a catalyst. This process is known as thermal cracking or pyrolysis. In this process, the substance is heated in the absence of air or oxygen to break the chemical bonds, leading to molecules with smaller sizes as shown in Figure 7 [76]. Vegetable oil can be converted to biofuel via pyrolysis, producing various amounts of carboxylic acids, alkadienes, alkenes, alkanes, and aromatics [77]. Especially in developing countries, thermal cracking is a costly process for producing biodiesel. The removal of oxygen throughout the thermal cracking process eliminates the environmental advantages of consuming an oxygenated fuel. Another disadvantage of thermal cracking is the need for distillation equipment in order to separate the fractions. Parawira [78] claimed that, similar to the gasoline, the product of pyrolysis process is less eco-friendly because it has sulfur in its composition. The pyrolytic chemistry can be quite difficult to distinguish, since various reaction products may be obtained from different reaction paths. Recently, petroleum has been produced from vegetable oil via pyrolysis method [79].

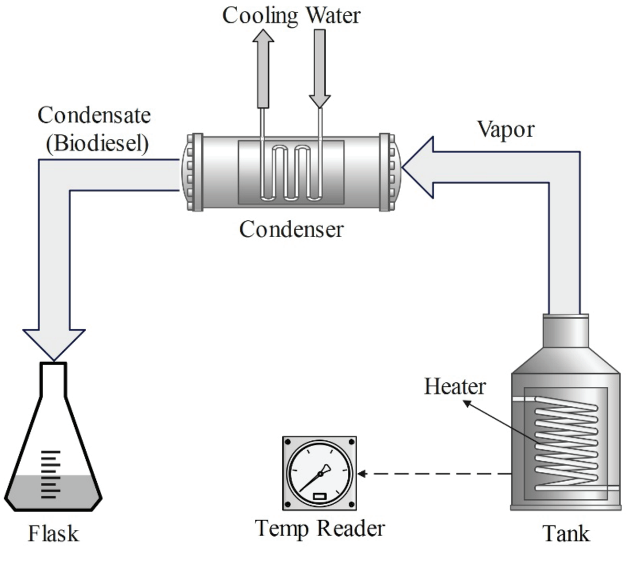


Figure 7. Schematic of biodiesel production by pyrolysis of WCO.

Transesterification method

During biodiesel production, methyl esters and glycerin are produced from triglycerides due to the exchange of esters by methanol. This results in methyl esters with lower viscosity than triglycerides and better efficiency as diesel fuel. In addition, the reaction between the triglyceride molecule and a low molecular weight alcohol results in the formation of three monoalkyl ester molecules and a by-product, i.e. glycerin molecule [72]. Strong alkaline or acidic catalysts can considerably increase the reaction rate. Generally, alkaline catalysts can decrease the reaction time. However, high concentration of free fatty acid in the oil results in an unwanted soapy reaction in the presence of alkaline catalysts. In this cases, acidic catalysts are usually used to solve the problem [80]. The best method for biodiesel production can be ester exchange. Generally, biodiesel is commercially produced by using alkaline catalysts under mild conditions, since they provide maximum production efficiency at the shortest reaction times with minimum side reactions. Transesterification is extensively used to obtained products with lower viscosity than triglycerides [81]. The reversible reaction between oil and alcohol results in the formation of glycerol alkyl esters and fatty acid. In the stoichiometric reaction, the required alcohol/oil molar ratio is 3:1, however more alcohol is used to shift the reversible reaction toward the products [82]. In the transesterification reaction, although both ethanol and methanol can be used as alcohol, the latter is less expensive and more available, has better physical and chemical properties, shows better polarity, and contains shorter hydrocarbon chain [83]. In addition, more biodiesel fuel can be obtained from oil in the presence of methanol which has higher affinity for oil. This may be due to the fact that methanol requires less energy for the separation of OH- ion in comparison with ethanol and other long hydrocarbon chain alcohols [84]. It is worth mentioning that alcohol purity significantly affects the transesterification reaction rate. In the other words, high purity avoids the mixture from waxing, resulting in higher biodiesel production efficiency. In addition, increasing the alcohol/oil molar ratio leads to higher solubility of glycerin in alcohol, making the separation of glycerin more difficult. The residual glycerin in the solution shifts the reaction toward the reactants, hence the amount of ester is reduced [8]. In the beginning, alcohol has low solubility in the oil which limits the transesterification reaction. Oil immiscibility in alcohol can limit the reaction rate due to the insufficient oil mass transfer. Figure 8 shows the schematic of transesterification process.

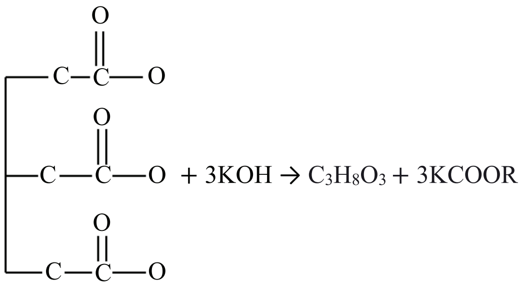
Furthermore, because of the inherent reversibility of the transesterification reaction, the conversion efficiency may be reduced if the product is not separated. The transesterification reaction rate may be significantly increased at shorter times in the presence of a proper solvent due to the formation of a single-phase system [85]. In such a case, the solvent increases the solubility, hence decreases the mass transfer resistance [86, 87]. On the other hand, the solvent recycling can be almost complicated. This problem can be solved by using a solvent (such as diethyl ether, tetrahydrofuran, etc.) with a boiling point similar to that of the alcohol. Tetrahydrofuran forms an oily single-phase system and considerably increases the methanolysis rate. Additionally, tetrahydrofuran can be easily recycled after transesterification because its boiling point is close to that of the methanol (67°C and 65°C, respectively) [85, 87]. Since oil has low miscibility in alcohol, vigorous stirring is required during transesterification reaction to completely disperse the alcohol in the triglyceride phase. Under these conditions, the mass transfer rate is improved which results in higher contact area between the oil and alcohol, thus increases the reaction rate and biodiesel efficiency. Otherwise, the reaction occurs only at the interface of the phases. Increasing the mixing intensity leads to higher reaction rate, hence decreases the reaction time [88]. Water content of raw materials is also affecting biodiesel production since esters are produced as a result of triglycerides hydrolysis in the presence of water and the formation of FFAs. In addition, FFAs create a soapy reaction medium which makes the product separation more difficult (due to formation of emulsion from biodiesel and soap) and hinders the catalytic activity. The free fatty acids and water contents in the oil have significant effect on the efficiency and catalytic activity [89]. Esterification reaction converts the free fatty acids to biodiesel by using an acidic catalyst.

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \qquad (1)$$

Under these circumstances, water can both decrease the catalytic activity and biodiesel production efficiency. However, if an alkaline catalyst is used during the esterification of free fatty acid (>0.5 wt%), the catalyst converts to soap [90, 91].

$$RCOOH + KOH \rightarrow RCOOK + H_2O \qquad (2)$$

FFA + Base → Soap + Water



$$\left[\begin{array}{l} -C-\overset{\overset{O}{\|}}{C}-O \\ -C-\overset{\overset{O}{\|}}{C}-O \\ -C-\overset{\overset{O}{\|}}{C}-O \end{array}\right. + 3KOH \rightarrow C_3H_8O_3 + 3KCOOR \qquad (3)$$

Triglyceride + Base → Glycerol + Soap

$$CH_3COOR + H_2O \rightarrow CH_3OH + COOHR \qquad (4)$$

Methyl Ester + Water → Methanol + FFA

Reactions 2, 3 and 4 describe free fatty acid soaping, triglyceride soaping, and methyl ester hydrolysis during the esterification reaction, respectively. Soaping reaction results in catalyst consumption and the need for removal of the impure soap. On the other hand, water formation also decreases the transesterification reaction rate [92]. Soap dissolution in the glycerol enhances biodiesel dissolution in the glycerol, makes the separation and purification of the product more difficult. The problem regarding free fatty acids can be avoided via a two-step process; acid transesterification step for removing free fatty acids, and a transesterification step for converting triglycerides to biodiesel [93, 94]. The oil type has significant effect on selecting the appropriate temperature of transesterification reaction which in turn affects the reaction rate. As reported in literature, transesterification reaction is generally performed at 60°C, but the reaction efficiency at different temperatures depends on the catalyst type. High reaction temperature can decrease the reaction time [95].

Transesterification via electrolysis

In recent years, researchers have focused on alternative methods for the production of biodiesel from recyclable materials. Catalyst-based electrolysis procedure could be a proper way for enhancing biodiesel yield [96]. Electrolysis may enhance the efficiency of biodiesel production from waste oils containing high concentrations of water and free fatty acids [89, 97]. In this method, transesterification reactions occur in one step due to the formation of H^+ and OH^- ions. Thus, in contrast to conventional biodiesel production methods, no soap reaction or destructive side reactions take place in electrolysis reaction. In addition, catalytic degradation does not occur at high FFA contents [98]. After addition of catalyst (low concentrations based on the oil weight) and H_2O to the electrolysis cell, hydroxyl and hydrogen are formed on the cathode while oxygen is oxidized on the anode. Reaction between hydroxyl ion and methanol leads to the formation of strongly nucleophilic methoxide ions which facilitate glyceride reaction with methanol, creating methyl esters and glycerol [99].

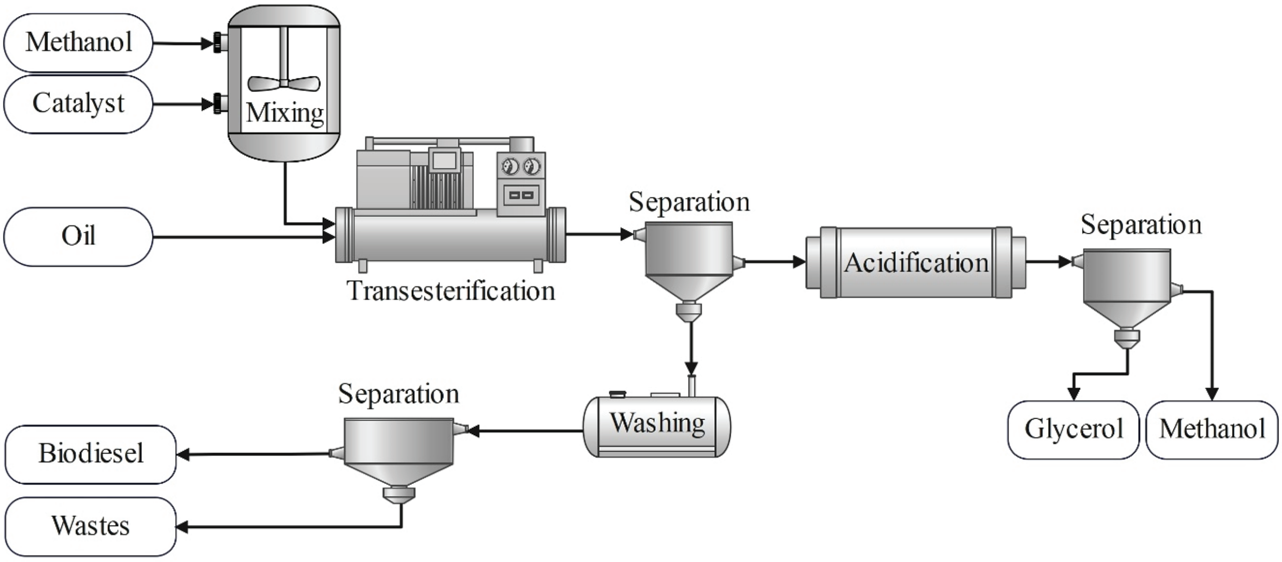


Figure 8. Schematic of biodiesel production via transesterification process.

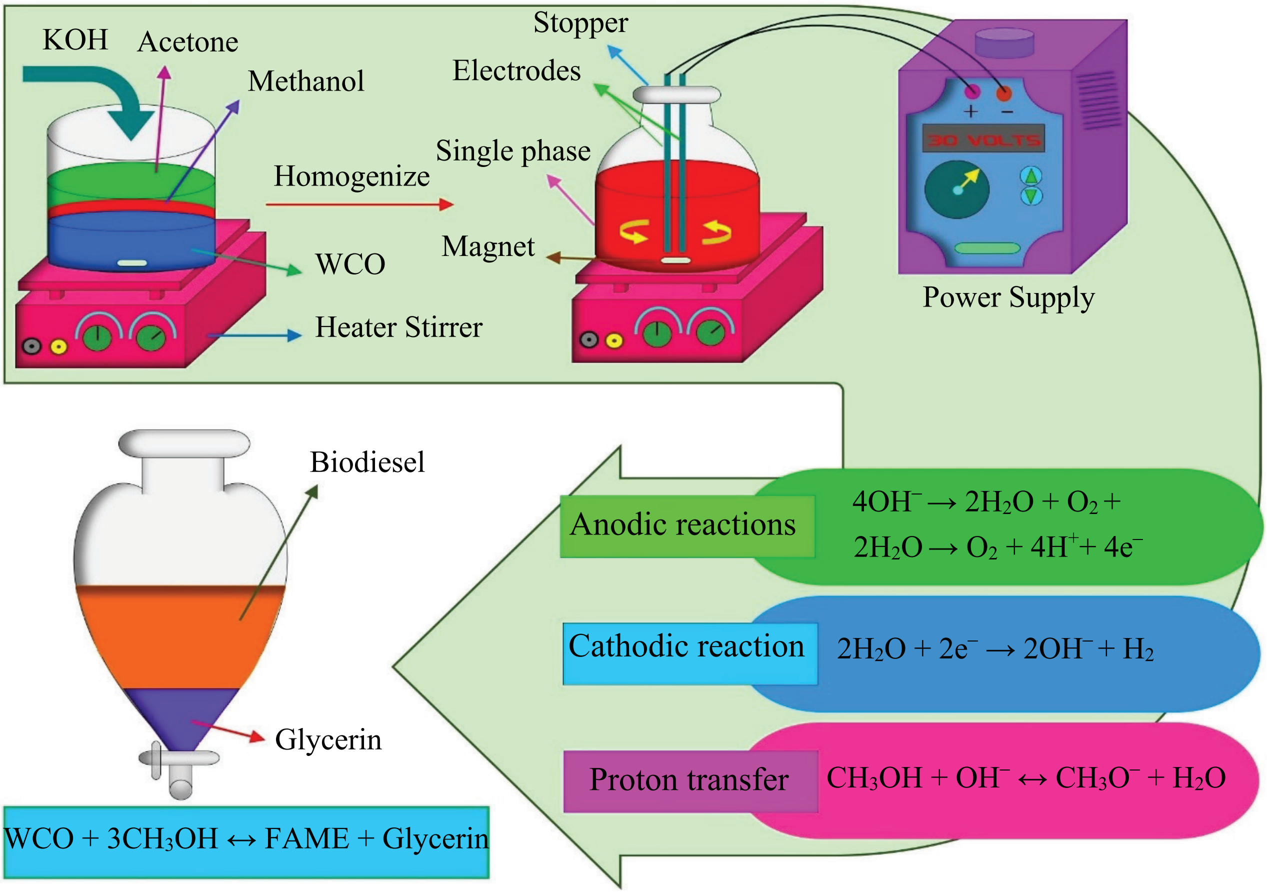


Figure 9. The schematic representation of the electrolysis process for biodiesel production using waste cooking oil (WCO) transesterification.

Electrolysis process has been performed for the transesterification of WCO in the presence of KOH catalyst. Biodiesel production efficiency of about 96% has been obtained after 2 h at room temperature at 50 v using methanol/oil molar ratio of 6:1, 2 wt% water, 0.5 wt% catalyst, and 10 wt% acetone (as solvent aid). The reactions were carried out at 25°C in order to reduce solvent and alcohol evaporation and decrease energy consumption [89]. Figure 9, schematically shows the electrolysis process and its reactions. Since the reaction is reversible, it is possible that the concentration of fatty acid methyl ester decreases over time. Thus, the time may have considerable effect on the concentration of fatty acid esters in the products [100].

In the electrolysis method, methanol is decomposed to methoxide ions in the presence of catalyst, which subsequently convert to reactive species for the transesterification reaction. Transesterification reaction occurs between triglycerides and short chain alcohols (such as methanol) in the following three consecutive steps: from triglycerides to diglycerides, monoglycerides, and finally to methyl esters and glycerol [101, 102]. Three moles of alcohol are consumed and one mole of ester is produced in transesterification [103]. Water molecules are removed rapidly from the reaction system by producing more active methoxide molecules. They also continuously decompose under the effect of electricity. Therefore, water plays a determining role in the electric charge transfer between the electrodes [104]. The catalyst concentration in the electrolysis cell influences the required energy or voltage for the initiation of chemical reactions at the electrode surface as well as the electric current in the reaction mixture. By increasing the applied voltage, the biodiesel production efficiency also increases, resulting in the formation of more hydroxide ions at the cathode which instantaneously react with the adjacent methanol molecules [105].

In the electrolysis process, biodiesel production performance increases at higher concentrations of OH^- ions and decreases at lower voltages [104]. Increasing the intensity of the mixture increases the level of contact between the oil and the methoxide and helps to create easy conditions for the reaction to begin. Without mixing equipment, the reaction occurs only at the interface of the phases. Therefore, with increasing mixing intensification with the help of solvent, the reaction rate increases and the reaction time decreases. The primary electrical conductivity is inversely proportional to the cosolvent/methanol molar ratio. Accordingly, the optimal cosolvent/alcohol molar ratio plays an important role in the production of biodiesel fuel via electrolysis method. Electrolysis in conjunction with heterogeneous catalysts facilitates some processing operations such as neutralization and separation. For example, in other biodiesel production methods, the product is washed three to four times, while in the electrolysis method, the required washing steps is decreased to one to two times. Biodiesel production efficiency of about 93% has been obtained via electrolysis for 3 h at 40 v using 1 wt% zeolite/chitosan/KOH composite as heterogeneous catalyst, graphite electrode, 2 wt% water, methanol/oil molar ratio of 7:1, and 10 wt% acetone as cosolvent aid at room temperature [50].

Homogeneous Alkaline and Acidic Catalysts for Biodiesel Production

In order to produce biodiesel, homogeneous acidic or alkaline catalysts are commonly used depending on the oil type and FFA content of the oil (Tables 2 and 3). Homogeneous alkaline catalysts (such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa) are superior to acidic ones for biodiesel production from low-FFA oils (generally, <0.5 wt% FFA) [15, 41]. Free fatty acids, in the presence of alkaline catalysts produce soaps, cause catalyst consumption, low FAAE yield, and more difficult separation. The FAEE production strongly depends on the initial concentration of alkaline catalysts. The optimum catalyst concentration, reported in the literature, is 1.0 wt%; however, in the case of NaOH, even lower (0.5%, 0.7% or 0.8%) and higher concentrations (6% or 3.3%) have also been used [106-109]. The maximum FAAE yield of 55% has been obtained with 3.3 wt% NaOH concentration [110]. Under similar operating conditions, a less amount of KOH catalyst (0.5 wt.%) gave the same yield as a higher amount of KOH catalyst (1.0 wt.%) [106]. The reported reaction times for transesterification, in the presence of alkaline catalysts, is usually in the range of 1-2 h; however, in some cases, it may last up to 5 h [111]. It has also been shown that the efficiency of biodiesel production from virgin oils is higher than that of waste frying oils (97% and 92%, respectively). Homogeneous alkaline catalysts are very sensitive to free fatty acid content. As a result, the free fatty acid content must be less than 0.5 wt%, to diminish soap formation during the transesterification in the presence of homogeneous alkaline catalyst [41].

In contrast, homogeneous acidic catalysts have less sensitivity to FFA in the raw material, because they can simultaneously catalyze both FFA and triglycerides. Some of the drawbacks of acidic catalysts are their low reaction rate, long reaction time, and high alcohol consumption, making them inappropriate for one-step biodiesel production methods [130]. The problems concerning biodiesel synthesis using high-FFA oils and homogeneous alkaline or acidic catalysts have been minimized by a two-step method (esterification and transesterification) [41, 131]. The first step is the esterification process using an acidic catalyst, to decrease the FFA content to less than 1%. The second step is the transesterification using an alkaline catalyst, to obtain biodiesel with high efficiency at short reaction times [132].

The effects of different homogeneous acidic catalysts (like H_3PO_4, sulfuric acid, BF_3, HCl, and organic sulfonic acids), oil type, and reaction conditions on one-step FAAE production are shown in Table 3 [133]. The unsatisfactory conversion yields have been reported using sulfuric acid and different alcohols (i.e. methanol, ethanol, and butanol)

Table 2. Effect of different homogeneous alkaline catalysts, oil type, and operating conditions on biodiesel production yield

Catalyst (wt%)	Oil	Alcohol/Oil Molar Ratio	Reaction time (min)	Temperature °C	Conversion/Yield (%)	Ref.
NaOH (0.6)	Sunflower	6:1	60	60	76-97	[112]
NaOH (1)	Sunflower	6:1	120	60	97.1	[113]
NaOH (1)	Palm	6:1	30	60	95	[114]
NaOH (1)	Jatropha	6:1	60	60	98	[107]
NaOH (0.8)	Jatropha	9:1	30	45	96.3	[109]
NaOH (3.3)	Jatropha	0.7:1	120	65	55	[110]
NaOH (0.7)	Neem	10:1	390-480	60-75	88-94	[115]
NaOH (3.4)	Microalgae	8:1	72	50	87.4	[116]
NaOH (1)	Tobacco seed oil	8:1	60	50	97	[106]
NaOH (0.6)	WFO	4.8:1	36	60	98	[117]
NaOH (1.1)	UFO	7.5:1	30	70	85.3	[118]
KOH (1.2)	WFO	6:1	120	60	95.8	[112]
KOH (1)	Karanja	6:1	120	65	98	[119]
KOH (1)	WFO	3:1	60	60	94	[120]
KOH (1)	Jatropha	6:1	120	50	97.7	[121]
KOH (0.5)	WCO	6:1	120	25	96	[89]
KOH (1)	WCO	7.5:1	120	25	98	[122]
KOH (0.7)	Mahua	6:1	55	60	95.7	[123]
KOH (0.7)	Mahua	6:1	30	60	98	[124]
KOH (0.6)	Cotton seed oil	6:1	60	55	96	[125]
KOH (1)	Palm kernel	6:1	60	60	96	[126]
CH_3OK (1)	Schleichera oleosa oil	8:1	90	55	91	[127]
CH_3ONa (0.8)	Cotton seed oil	6:1	90	65	96.9	[128]
CH_3ONa (0.7)	Rice bran	6:1	60	55	83.3	[129]

with alcohol/oil ratios of 6:1 and 20:1and the reaction times of 3 h and 18 h, respectively. In contrast, alcohol/oil molar ratio of 30:1 resulted in high conversion yield [134]. It can be seen form Table 3 that the high biodiesel yields (<90%) via transesterification in the presence of homogeneous acidic catalysts need higher temperatures, much longer reaction times, high quantity of alcohols, and more catalyst concentration [135]. Thus, transesterification of low-FFA oils using homogeneous acidic catalysts suffers from the following disadvantages: high alcohol consumption, low catalytic activity, low reaction rate, and high reaction temperature. Therefore, homogeneous acidic catalysts are best suited for biodiesel production via esterification of low-cost high-FFA oils. The conversion rate and yield of FFA into biodiesel significantly depend on the reaction temperature, the amount and type of alcohol, the concentration and type of catalyst, and the initial FFA content. Also, it is found that, for the same catalyst (H_2SO_4) and its amount (1 wt.%), oil (Castor oil), and reaction temperature (50°C), the biodiesel yield is higher (90.83%) for the case where the molar ratio of alcohol/oil is (20:1) [136, 137].

Heterogeneous Alkaline and Acidic Catalysts for Biodiesel Production

It seems that solid catalysts can be a promising alternative to homogeneous catalysts in transesterification reactions, since they are reusable and less corrosive. In addition, they can be more easily separated from the reaction medium and produce less toxic residuals. Similar to homogeneous catalysts, heterogeneous catalysts are also influenced by factors such as water content, FFA levels, and the type of oil used as feed [146, 147]. Heterogeneous catalysts can prevent undesirable soaping in transesterification reaction and tolerate more aggressive operating conditions (high pressure and temperature). They also eliminate some operating steps, which are performed for homogeneous catalysts; thus, simplify the transesterification process and reduce the production costs [148].

Heterogeneous catalysts show better performance than homogeneous ones for high-FFA oils. Typically, solid heterogeneous catalysts can be alkaline, acidic, or bifunctional (acid-base). Solid acidic catalysts can catalyze esterification reaction, while alkaline solid catalysts can catalyze transesterification reaction. On the other side, bifunctional solid

Table 3. Effect of different homogeneous acidic catalysts, oil type, and operating conditions on biodiesel production yield

Catalyst (wt%)	Oil	Alcohol/ Oil Molar Ratio	Reaction time (min)	Temperature °C	Conversion/Yield (%)	Ref.
HCl (10)	Rice bran	20:1	2700	70	65	[138]
HCl (10)	Soybean	20:1	240	60	90	[138]
H_2SO_4 (0.5)	Soybean	9:1	480	100	99	[139]
H_2SO_4 (5)	WCO	12:1	180	60	95.3	[101]
H_2SO_4 (4)	WCO	20:1	600	95	90	[140]
H_2SO_4 (1)	Castor oil	20:1	60	50	90.8	[137]
H_2SO_4 (1)	Castor oil	15:1	125	50	73.2	[136]
H_2SO_4 (6.5)	Used soya been	12:1	600	65	75.7	[141]
H_2SO_4 (4)	WCO	20:1	600	95	90	[140]
H_2SO_4 (1)	WFO	14.7:1	60	60	93.3	[142]
H_2SO_4 (1)	Tobacco	18:1	24	60	91	[143]
H_2SO_4 (10.7)	Rubber seed oil	10:1	60	65	98.6	[144]
H_2SO_4 (0.5)	Rubber seed oil	6:1	30	40-50	98	[145]

catalysts can concurrently catalyze both the esterification and transesterification processes [41, 149]. In the case of biodiesel production, using heterogeneous catalysts, more catalyst is needed at higher alcohol/oil molar ratio, which increases the required temperature and pressure. In addition, three phases are formed with oil and alcohol, which make the diffusion more difficult; hence, decrease the reaction rate. This problem can be solved by using an auxiliary cosolvent to improve the miscibility of oil and alcohol, thus increasing the reaction rate [150, 151]. Most of alkaline heterogeneous catalysts consist of alkalis and alkaline oxides with high specific surface area. Therefore, similar to homogeneous catalysts, solid heterogeneous alkaline catalysts have higher activity than solid heterogeneous acidic catalysts. As an example, CaO has a long catalytic life and activity, but its reaction rate for biodiesel production is low. In addition, it has low solubility in alcohol, which could be prepared by inexpensive sources such as CaO and limestone; hence, it is more environmentally friendly [152]. Granados et al. [153] performed methanolysis of sunflower oil using activated calcium oxide as catalyst. They also studied the effect of water and CaO on the catalytic activity at different time intervals. They reported that hydration and carbonation of calcium oxides occurs rapidly in air, and no CaO peak could be detected after 20 days. This means that the surface of calcium oxide is saturated with water and carbon dioxide molecules. For this reason, calcium oxide should be heated at 700°C before use, to remove the adsorbed carbon dioxide from the surface of the catalyst; hence, improving its catalytic activity.

Figure 10 shows the transesterification steps for the production of biodiesel using CaO. The first step is the CaO dissociation with methanol to produce protonated (H^+) catalyst and methoxide anion ($CH3O^-$). The generated $CH3O^-$ nucleophilically attacks carbonyl carbon of triglyceride, resulting in the generation of a tetrahedral intermediate. Upon the rearrangement of molecules in the intermediate compound, a mole of methyl ester is formed together with the diglyceride anion. The deprotonation of catalyst causes the regeneration of active species for the next catalytic cycle, i.e. reaction with the second methanol molecule. The $CH3O^-$ would attack another carbonyl carbon atom in the generated diglyceride and forms another mole of methyl ester together with monoglyceride. Finally, the monoglyceride is similarly converted to alkyl ester and glycerol [20, 154].

Nanocrystalline calcium oxides have higher efficiency than the conventional calcium oxides. For example, 100% conversion of soybean oil has been achieved using 20 nm calcium oxide nanocrystals and specific surface area of 90 m^2/g at the ambient temperature after 12 h. While the conversion rate for the commercial calcium oxide was 100%. With a crystal size of 43 nm and a specific surface area of 1 m^2/g, it was only 2% [155]. It has been reported that the catalytic activity and biodiesel efficiency of calcium oxide could be improved in the presence of water, since the presence of water and O^{2-} on the surface removes H^+ from the water molecule. Then, OH^- is produced, which removes H^+ from methanol, and the methoxide anion, which is the real catalyst, is produced for the ester exchange reaction. Addition of 2.03% water to the reaction medium containing alcohol/oil molar ratio of 12: 1 and 8 wt% catalyst resulted in 95% methyl ester yield after 3 h; while in the absence of water, it reached 80%. No active phase output was observed in the reaction medium and the catalyst could be reused up to 20 times [156]. Strontium oxide is an efficient solid alkaline catalyst for the conversion of soybean oil. In spite of its low specific surface area (1.05 m^2/g), 90% of the soybean oil could be converted to methyl ester after 30

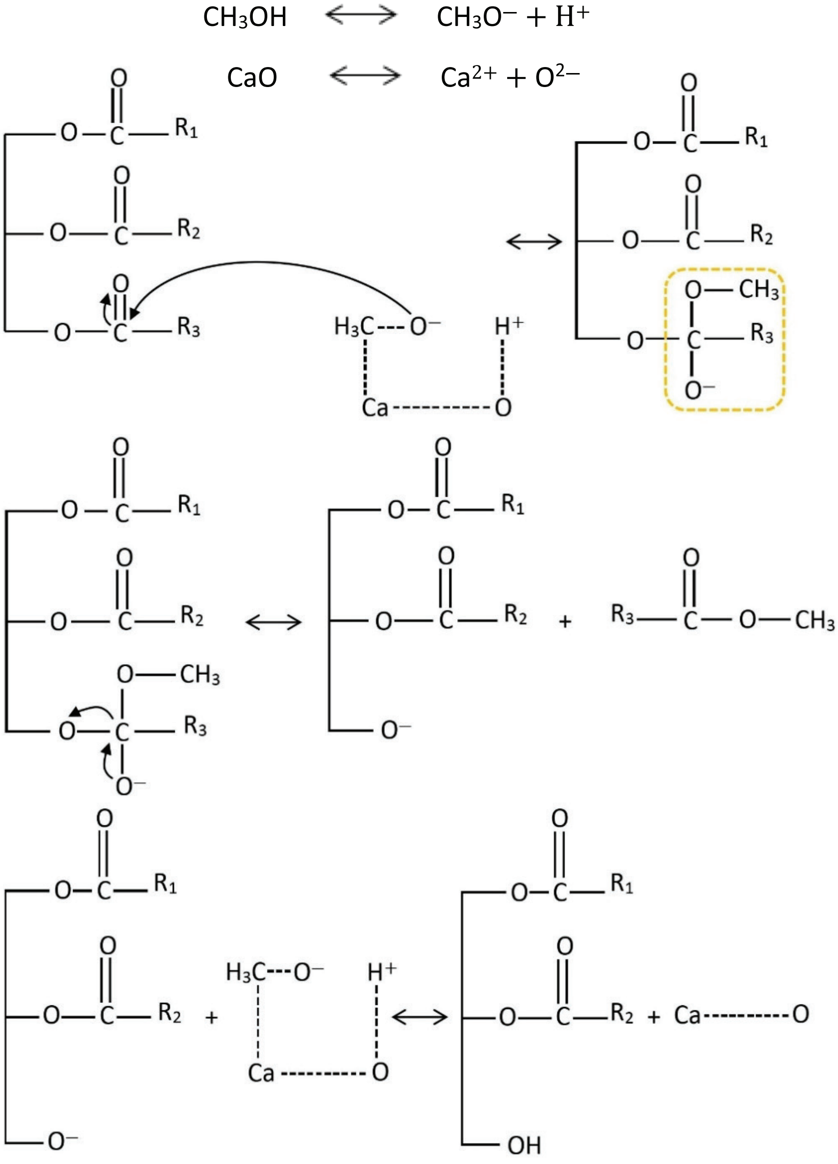


Figure 10. Triglyceride transesterification mechanism using CaO as catalyst.

min at 65°C using an alcohol/oil molar ratio of 12 and 3 wt% catalyst [157]. Xie et al. [158] investigated the catalytic activity of potassium-deposited alumina as solid alkaline catalyst for the production of biodiesel from soybean oil. They produced the catalyst via an aqueous solution impregnation of potassium nitrate on alumina. The best activity was obtained for 35 wt% potassium nitrate catalyst calcined at 500°C.

Xie and Li [159] utilized alumina coated with potassium iodide as an alkaline catalyst for methanolysis of soybean oil. They investigated the dependency of conversion rate on potassium iodide concentration and calcination temperature. The best catalytic activity was reported for 35% potassium iodide and calcination temperature of 500°C for 3 h. Kim et al. [160] used alumina coated with sodium and sodium hydroxide as a solid alkaline catalyst, to convert oil to biodiesel using a mixture of methanol and hexane. First, they mixed γ-alumina, sodium metal, and sodium hydroxide, and then, heated the mixture in a stainless steel reactor at 320°C. This method led to the reduction of γ-alumina specific surface area from 143.1 to 83.2 m^2/g. Yang and Xie [161] investigated the catalytic activity of alkaline earth metals for the conversion of soybean oil to biodiesel and also the dependency of oil conversion on the amount of active phase loading. They reported that the concentration of surface sites on the catalyst significantly affected the catalyst efficiency. Among the synthesized catalysts, $ZnO/Sr(NO_3)_2$ exhibited the best catalytic activity. The maximum catalytic activity was obtained with 2.5 mmol strontium nitrate loaded on zinc oxide, corresponding to the basicity of 10.8 mmol/g. Xie and Huang [162] used potassium-coated ZnO as solid alkaline catalyst. Based on the Hammett indicator method, the surface basicity of 1.47 mmol/g was obtained for 15 wt% potassium fluoride loaded on the zinc oxide, and 87% of soybean oil was converted after 9 h using 3 wt% catalyst and alcohol/oil ratio of 10:1.

Sayed et al. [163] performed transesterification of sunflower WCO in the presence of a novel geopolymer, which was synthesized using natural silica resources and synthetic MgAl-layered double hydroxide (MgAl-LDH) nanostructures as a promising heterogeneous potassium-loaded catalyst. The suggested mechanism for transesterification of sunflower oil for the production of biodiesel is depicted in Figure 11. After the adsorption of methanol onto the surface of catalyst, the hydrogen in methanol reacts by the potassium. Then, the ion exchange between potassium and methanol results in the formation of CH_3O- alkoxide anion. On the other side, the terminated –OH groups physically bond with part of the fatty acid on the surface of the catalyst and form a protonated carbonyl group, which is attacked by the CH_3O- ion, producing the corresponding ester. Methanol is highly acidic, thus, the presence of methoxide moieties on the surface of the catalyst is indicative of the formation of alkoxide anions. Meloni et al. [164] proposed that the basic site could catalyze the transesterification reaction,

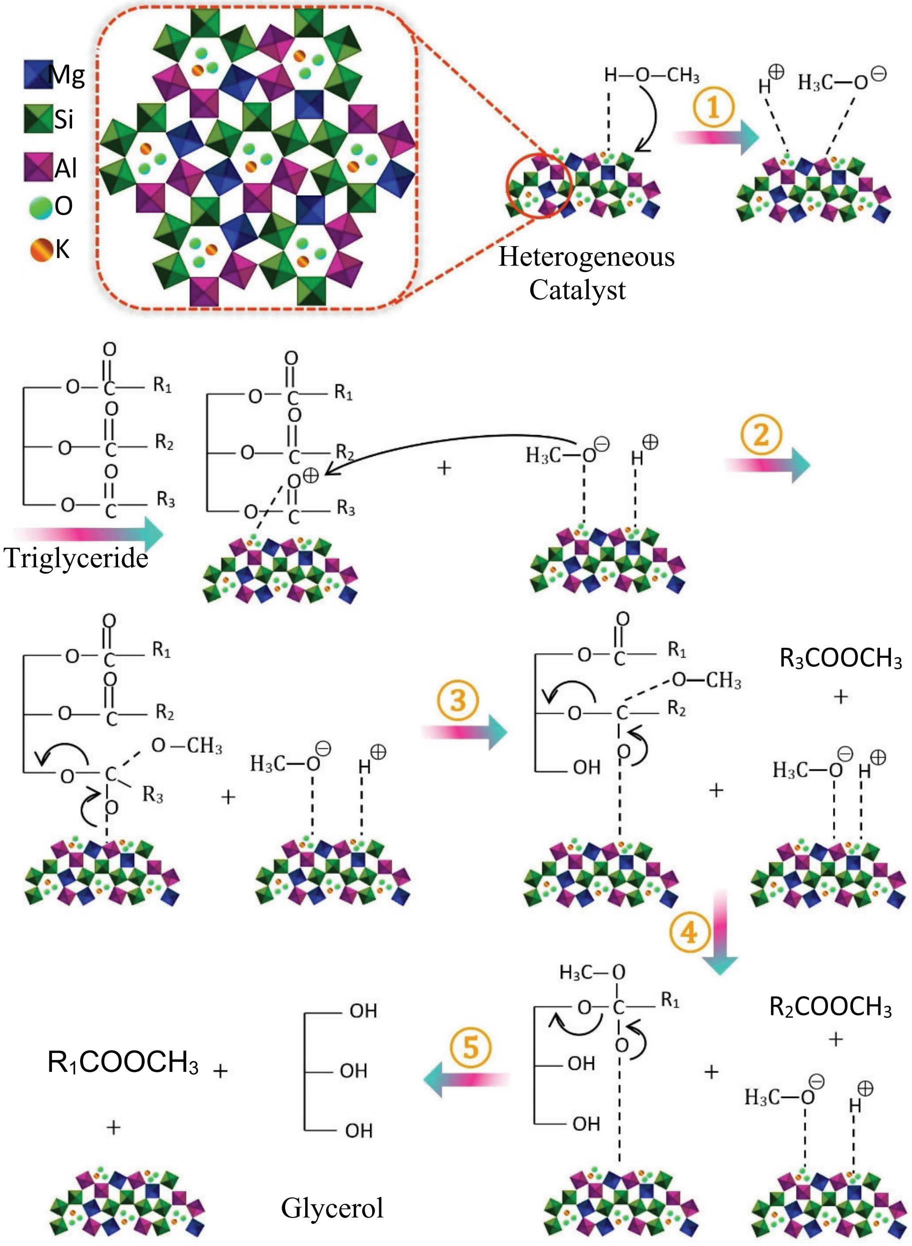


Figure 11. The transesterification mechanism for biodiesel production from sunflower oil using MgAl-LDH based potassium/geopolymer.

providing that the presence of some acidic site stabilizes the abstracted proton from methanol to get stable methoxy species. According to the test results, the best experimental conditions for achieving 94.6% biodiesel yield were the reaction time of 4 h, reaction temperature of 120°C, catalyst concentration of 4 wt%, and methanol/oil ratio of 15:1.

It was also reported that zeolites are alkaline due to the neutralization of negative lattice charge by alkali metals, which increases the electron density of the lattice oxygen, the strength of which depends on the chemical composition, network structure, and the nature of interactions. The adsorption of charged alkali metal clusters of Na increases the zeolite basicity through increasing the negative charge of the lattice oxygen. The species are inserted into the zeolite pores via wet impregnation using an aqueous solution containing precursor. The adsorbed compounds are decomposed during the calcination step, leaving alkali metal oxides on the substrate [165]. Xie et al. [166] used NaX zeolite, impregnated with KOH as solid alkaline catalyst, for transesterification reaction of oil in the presence of methanol. The catalyst was impregnated using an aqueous solution with different potassium hydroxide loadings for 24 h, in order to homogeneously disperse the potassium hydroxide on the surface of zeolite. The samples were dried in a rotary drier, and then, calcined at 120°C for 3 h. Under these circumstances, the best efficiency (85.6%) was obtained at 65°C for 8 h using 3 wt% catalyst, 10 wt% potassium hydroxide loading on the zeolite, and alcohol/oil molar ratio of 10:1. After catalyst recycling, it was revealed that potassium hydroxide has been removed from the zeolite structure and a relatively homogeneous reaction has occurred, leading to a decrease in the performance of the recycled catalyst.

A similar investigation has been carried out by Wang and Chen [167] who synthesized beta zeolite with high Si/Al ratio as heterogeneous catalyst via hydrothermal method for transesterification of triolein into biodiesel. They suggested that Na cations in the cages and defects of the beta zeolite could act as catalyst during transesterification reaction; thus, increasing the production efficiency. In addition, the lattice oxygen atoms together with the surface sodium result in the surface electronegativity of zeolite. Figure 12 schematically shows the transfer of Na^+ from the defect sites or the intrapores of the Na-BEA to the surface of the zeolite support and silicate [167]. As a result, the absence of active sodium species on the surface of catalyst could be the main reason for catalyst deactivation.

Ramos et al. [168] performed transesterification of sunflower oil on different zeolites like mordenite, beta zeolite, and X zeolite to investigate the influence of zeolite type on the methyl ester production efficiency. They also examined the effect of alkaline ions incorporated via ion exchange and impregnation approaches. They found that the impregnation is slightly superior to ion exchange method. In the case of X zeolite agglomerated with sodium bentonite, the production efficiency was 93.5%, while that of X zeolite without sodium bentonite was 95.1%. Kim et al. [169] synthesized $ZnO-Al_2O_3/ZSM-5$ and $SnO-Al_2O_3/ZSM-5$ catalysts for transesterification of soybean oil with methanol. They also studied the effect of sodium on the catalytic activity of the synthesized catalysts. ZSM-5 zeolite substrate was prepared via hydrothermal method, and then, calcined at 650°C for 2 h. Metal oxides were deposited on the ZSM-5 substrate through impregnation of metal salt solutions. They added $Zn(NO_3)_2$ and $Al(NO_3)_3$ solutions, and a solution containing tin chloride and aluminum nitrate to ZSM-5 zeolite The as-synthesized $SnO-Al_2O_3/ZSM-5$ catalyst showed 45% fatty acid methyl ester (FAME) efficiency after the reaction time of 9 h. However, after two washing steps, the catalytic activity significantly reduced to 10% FAME. The catalyst showed no activity after three washing steps. In the case of unwashed $ZnO-Al_2O_3/ZSM-5$ catalyst, high catalytic activity (98% FAME) was achieved after 9 h. However, after two washing steps and 9 h reaction time, the efficiency reduced to 39.3% FAME. More washing steps resulted in further decrease in the catalytic activity. Sedaghat-Hoor and Anbia [170] synthesized MgAl(O) catalyst via co-precipitation method followed by ZnO impregnation and calcination. They used the synthesized catalyst for biodiesel production through transesterification of WCO. According to Figure 13, in the case of co-precipitated product, only the layered platelet structure is available for the transesterification. However, in the case of Zn/MgAl(O), synthesized via co-precipitation followed by impregnation, both layered and nanoparticle structures take part in transesterification, resulting in a higher efficiency (78.45% FAME) at 65°C using 9:1 methanol/oil ratio for 3 h.

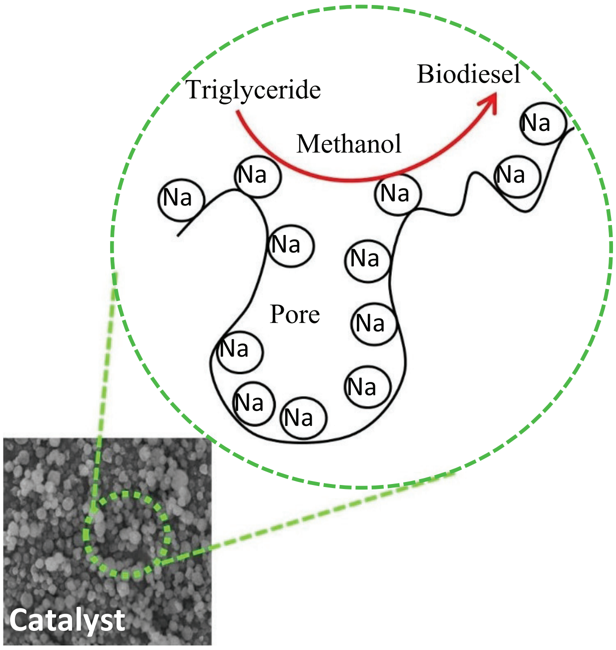


Figure 12. Schematic representation of triolein transesterification for biodiesel production using Na-treated zeolite catalyst.

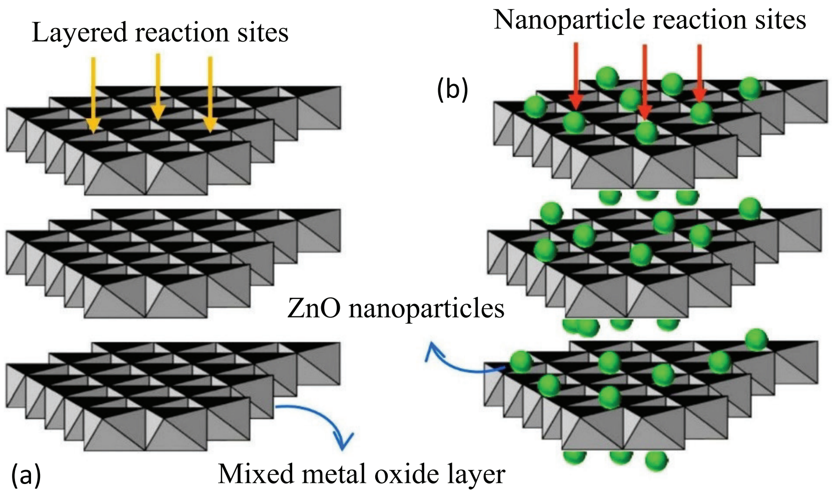


Figure 13. Schematic representation of active sites in (a) co-precipitated ZnMgAl, and (b) Zn/MgAl(O) [170] [Open Access].

Solid acidic catalysts have less sensitivity to free fatty acids and moisture in comparison with liquid acidic catalysts. As a result, low quality feeds can be used for biodiesel production in the presence of such catalysts. In addition, it is possible for esterification and transesterification reactions to be carried out concurrently using acidic solid catalysts. Recycling and reusability of heterogeneous acidic catalysts result in less wastewater production. Medium to strong acidity, large cavities, and hydrophobic surface are crucial for biodiesel production by using solid acidic catalysts. Esterification efficiency strongly depends on crystalline phases, size of cavities, and acidity. Solid acidic catalysts have also less environmental pollution and corrosion problems than strong liquid acids [171]. In spite of their low activity, solid acidic catalysts are widely used in several industrial applications because they have more acidic sites with different Brønsted and Lewis acidity strengths in comparison with homogeneous acidic catalysts.

There are numerous reports on the application of zirconia as solid acidic catalyst instead of other transition metal oxides for biodiesel production from different oils. This may be due to the high acidity of the zirconia and the fact that the acidity enhances in the presence of anions like sulfate (SO_4^{2-}) and tungstate (WO_4^{2-}) on the surface of metal oxides. López et al. [172] compared the catalytic activity of highly acidic ZrO_2/SO_4^{2-} and ZrO_2/WO_3^{2-} catalysts for the methanolysis of triacetin. Their findings indicate that the specific surface area and the concentration of active sites play a significant role in catalytic activity. The results showed that ZrO_2/SO_4^{2-} has higher activity than ZrO_2/WO_3^{2-} after the reaction time of 8 h at 60°C. The reason for this observation is the higher specific surface area of ZrO_2/SO_4^{2-} compared with ZrO_2/WO_3^{2-} (134 and 89 m^2/g, respectively). In addition, ZrO_2/SO_4^{2-} had more active sites than ZrO_2/WO_3^{2-} (94 and 54 μmol/g, respectively). In another study carried out by Chen et al. [173], catalytic activity of $TiO_2/\ SO_4^{2-}$ and $ZrO_2/\ SO_4^{2-}$ as strong solid acidic catalysts were examined for transesterification of cottonseed oil. The results showed that the catalytic activity of $TiO_2/\ SO_4^{2-}$ is higher than that of $ZrO_2/\ SO_4^{2-}$ mainly due to its higher specific surface area (99.5 and 91.5 m^2/g, respectively). They also found that new Lewis and Brønsted acid sites have been formed on the surface of catalyst in the presence of sulfate anions. Methyl ester yield after 8 h reaction using 2 wt% of $TiO_2/\ SO_4^{2-}$ and ZrO_2/SO_4^{2-} catalysts and alcohol/oil molar ratio of 8:1 was 90% and 85%, respectively.

Ramu et al. [174] investigated the effect of calcination temperature and WO_3 loading on the catalytic activity of ZrO_2/WO_3^{2-} for esterification of palmitic acid in the presence of methanol. They observed the highest catalytic activity for the catalyst calcined at 500°C owing to the formation of tetragonal ZrO_2 phase. Calcination above 500°C resulted in the transformation of tetragonal to monoclinic phase. For example, 98% palmitic acid conversion efficiency reduced to 8% after calcination at 900°C. On the other hand, acidic sites concentration of 1.04 mmol/g was obtained by loading 5 wt% WO_3. However, at higher WO_3 loadings, the catalytic activity decreased because of more coverage of ZrO_2 surface by WO_3. Conversion of soybean oil using tungstated zirconia (WO_3/ZrO_2) has been also studied by Furuta et al. [175]. They achieved 94% oil conversion after 8 h reaction at 300°C using alcohol/oil ratio of 40:1. The catalyst was active up to 100 h reaction. In addition, WO_3/ZrO_2 (WZO) showed higher activity for soybean conversion in comparison with sulfated zirconia (SO_4/ZrO_2) (SZO) and sulfated tin oxide (SO_4/SnO_2) (STO) which yielded 70% and 80% conversion efficiency, respectively.

Fe-Zn double-metal cyanide (DMC) complexes have been applied as solid acidic catalyst for methanolysis of sunflower oil [176]. It has been reported that the oil conversion efficiency of 97% is achievable via transesterification at 170°C for 8 h using 0.3 wt% catalyst and alcohol/oil ratio of 15:1. They found that the catalytic activity may arise from the Lewis acid active sites owing to the presence of Zn^{2+} ions on the surface of the catalyst. In addition, the catalyst was able to convert oil with 20 wt% water which implies that the catalyst has hydrophobic surface. The catalyst also showed reasonable performance for esterification of oils containing high amounts of free fatty acids even after several cycles. Jacobson et al. [177] utilized various solid acidic catalysts including MoO_3/SiO_2, TPA/ZrO_2, $WO3/ZrO_2$-Al_2O_3, WO_3/ZrO_2, MoO_3/ZrO_2, zinc stearate/SiO_2, and zinc ethanoate/SiO2 for the production of biodiesel from WCO. The reactions were carried out at 200°C for 10 h using 3 wt% catalyst and alcohol/oil molar ratio of 18:1. The maximum production efficiency of 98% was achieved for zinc stearate catalyst on silica gel (SiO_2) support which was synthesized via sol-gel method. The catalyst was reusable even after several catalytic cycles. Chung et al. [178] employed a variety of zeolite catalysts including mordenite (MOR), beta (BEA), faujasite (FAU), and ZSM-5 (MFI) zeolites as well as with different Si/Al molar ratios for removing free fatty acids from WCOs via esterification in the presence of methanol. The reaction was conducted at 60°C for 3 h using 1 g catalyst and alcohol/oil ratio of 30:1. The maximum FFA removal efficiencies of 78% and 80% were obtained for ZSM-5 and MOR catalysts, respectively, while silicalite showed the lowest efficiency mainly due to its very weak acidic sites. Although HMOR(10) has more acidic sites and higher acid strength than HMFI(25), they showed similar removal efficiency. The reason for this is that MFI has finer pores with zigzag structure, leading to the cracking of the reactant with long chain, while MOR has straight channels with wide pore opening. Furthermore, at higher Si/Al ratios, the acidic sites decreased in the zeolite, resulting in lower FFA removal efficiency.

Karmee and Chadha [179] produced biodiesel from inedible Pongamia pinnata oil via transesterification in the presence of methanol and KOH catalyst. The reaction was performed at 60°C for 1.5 h using alcohol/oil molar ratio of 10:1 and 1 wt% KOH. They also employed solid acidic catalysts (i.e. Hβ zeolite, K-10 montmorillonite, and zinc oxide) for transesterification reaction at 120°C for 24 h using alcohol/oil molar ratio of 10:1 and 10 wt% catalyst. The conversion efficiency for zinc oxide, Hβ zeolite, and K-10 montmorillonite catalysts was 83%, 59%, and 47%, respectively, while that of potassium hydroxide was 92% which increased to 95% by the addition of tetrahydrofuran cosolvent. Shu et al. [180] synthesized lanthanum-modified beta zeolite catalyst via ion exchange method by stirring 10 g beta zeolite in 250 ml of 0.1 M $La(NO_3)_3$ solution for 3 h at room temperature followed by filtering, washing with deionized water, drying at 20 ˚C, and at last calcination at 523°C for 4 h. The synthesized catalyst was employed for biodiesel production at 60°C for 4 h using alcohol/oil ratio of 14.5 and catalyst/oil weight ratio of 0.011, resulting in 48.9 wt% triglyceride conversion. Due to the small pore size of beta zeolite, triglyceride molecules have limited access to the internal acidic sites. Thus, the catalytic activity mainly arises from the external acidic sites on the surface of the beta zeolite. On the other hand, lanthanum creates a lot of Brønsted acid sites which are available for the reactants, resulting in an increase in triglyceride conversion efficiency by 10 wt%.

Recovery of Biodiesel Purification By-products

In order to increase the productivity of the biodiesel process, it is possible to convert the by-products into more valuable products [181]. One of these by-products is crude glycerol because of its high concentration (8-10%) in transesterification process. It has been predicted by Rastegari et al. [182] that about 41.9 billion liters of glycerol will be globally produced by 2020. Monteiro et al. [183] reported that pure and crude glycerol (80% purity) cost 0.60-0.91 and 0.09-0.20 USD/kg, respectively. A number of industries such as food, cosmetics, pharmaceuticals, textile, fuel additives, and medicine can utilize pure glycerol as raw materials, hence increasing the economic efficiency of biodiesel production [184]. Garlapati et al. [185] proposed biological conversion of crude glycerol to other valuable products using microbes. Purification of the produced biodiesel (i.e. separation of excess alcohol, remaining oil, catalysts, and glycerol) after transesterification is crucial to increase the performance and protection of the engine by using high quality biodiesel. As reviewed by Veljkovićet al. [186], there are a range of methods for biodiesel purification in addition to reactive distillation and centrifugal contractor methods such as dry washing, wet washing, precipitation, membrane filtration, liquid–liquid extraction, vacuum distillation, and column chromatography. The selection of which mainly depends on the type of catalyst. In wet washing method, biodiesel produced by homogeneous alkaline catalysts is first washed with acidic and then with neutral water to remove water-soluble impurities such as glycerol and residual methanol. Due to the formation of stable calcium soap, this method is not recommended for the production of biodiesel using heterogeneous catalysts (such as CaO) [187]. In precipitation method, different precipitant agents such as citric acid and oxalic acid are used to precipitate calcium ions (in the case of reactions heterogeneously catalyzed by CaO). Each gallon of biodiesel generates almost one pound of glycerol, thus there are extra glycerol at low prices produced by biodiesel industries [188]. On the other hand, the impurities in the crude glycerol (for example, glycerides, solvents (methanol), soap, etc.) prevent its direct exploitation. Bhatia et al. [133] applied neutralization, exchange resin and microfiltration methods for purification of crude glycerol. Filtration, saponification, evaporation, phase separation and neutralization methods have been also employed to obtain glycerol with 86% purity. Other impurities like color variation of biodiesel could be adjusted via reaction parameters and the catalysts [189].

Crude glycerol has been recovered in laboratory up to 93.3% purity via combination of repeated physical and chemical steps including phase separation, acidification, solvent extraction and neutralization [190]. Conversion of the recovered glycerol into other value-added bioproducts can be conducted via different microbial processes or physicochemical reactions. Yuksel et al. [191] employed hydrothermal electrolysis for the conversion of glycerol into lactic acid under aqueous alkaline conditions at high temperature and pressure. Samudrala et al. [192] activated montmorillonite with sulfuric acid and used it as support for platinum catalyst for hydrogenolysis of glycerol into 1-3 propanediol. Other biochemicals such as lactic acid, citric acid, 1-3 dihydroxyacetone, 1-3 propanediol, biohydrogen, ethanol, etc. can be produced via microbial fermentation of glycerol c.

Challenges and Limitations of Biodiesel Production

In spite of intense research on new raw materials, oil conversion technologies, biodiesel processing, there are many limitations and barriers which should be overcome for cost-effective biodiesel production on industrial scale. Some of these challenges and the corresponding solutions are discussed below [193].

Feedstock limitations

At present, the production cost of biodiesel is higher than that of fossil fuels. Biodiesel is mostly produced from crops because they can be easily processed, but there is a growing market competition between food and fuel. The annual crop productivity is strongly affected by the environmental conditions and other parameters. It is not possible to grow all types of feedstock in all regions of the world. Thus, transportation of feedstock is costly. Since oil extraction faces some challenges, utilization of animal fats, WCO, and microalgal oil has not sufficiently developed. Moisture and FFA content may cause some problems; water may increase microbial growth, and FFA should be removed by pretreatment [194]. Furthermore, effective risk management is not possible due to the insufficient development of feedstock market. Accordingly, the price of biodiesel is not as manageable as that of fossil fuels. Continuous production of biodiesel needs locally available feedstock all over the year with easy collection and transportation and minimum processing requirements.

Technological and financial limitations

Reusable catalysts, management of by-products, and downstream biodiesel processing are other technical challenges for cost-effective production of biodiesel. In addition, more processing plants with acceptable performance and novel technologies are required. New technology requires extensive field and demonstration to make it acceptable to investors and users. Biodiesel production has also financial risks because of the lag time between investment and return. The profit is highly dependent on the government policies. Biodiesel production principles are well-known theoretically, but its execution on industrial scale needs further information and novel strategies for cost-effective biodiesel production.

Infrastructure

The new field of biodiesel production needs heavy investment for new infrastructure, skilled labor, distributors, storage, and transportation. Unlike developed industries, the insufficient development of biodiesel industry prevents its integration with other processes. For these reasons, investors only will to invest in fast-growing industries with good returns, thus limiting biodiesel industry to small scale plants [195].

Customer demand and approval

Lack of enough knowledge on the performance and benefits of biodiesel, its high cost, and the lack of government policies and support are some reasons that have led to low demand for biodiesel. The economic conditions of rural people can be improved by making them aware of the role of biodiesel in energy security and environmental protection. For gradual development and commercialization of biodiesel, people should be convinced to use biodiesel.

Government support

Different countries have set policies to promote and adapt biofuel applications. Government has tried to increase biofuel consumption and production by applying mandate and tax exemption. It is planned that the USA will use 36 billion gallons of renewable fuel in its transportation sector by 2022, for instance. The climate and energy objectives to 2030 set by European Union (EU) includes reducing up to 40% greenhouse gases and increasing the renewable energy share in all sectors to 32%. The Indian National Policy on Biofuels in 2008 necessitates blending of 20% biodiesel and bioethanol with gasoline by 2017. Additionally, it was intended to plant Jatropha on 11.2 million hectares of wasteland. In 2005, Malaysia's National Biofuel Policy mandated that 5% of palm oil be used for biodiesel. It is important to consider a number of factors, including infrastructure, emission, feedstock availability, performance, compatibility with automobiles engine, etc. are some of the key parameters that should be considered for future biodiesel production [196].

CONCLUSION

Rising demand for alternative fuels, particularly biodiesel, is driven by the need to reduce fossil fuel dependence, address health and environmental concerns, and meet growing energy demands. This article provides a comprehensive exploration of recent biodiesel production advancements, encompassing key aspects such as biodiesel properties, various feedstocks (with a particular focus on waste cooking oil), synthesis methods, catalysts, advanced enhancement techniques, and associated challenges. Biofuel can be a promising alternative to conventional fossil fuels due to its low toxicity, biodegradability, and similar performance to fossil fuel. Commercial production of fatty acid methyl ester (FAME) is currently the only solution for the global energy demand. On the other hand, FAME production methods are not efficient due to the need for catalyst separation and the high production cost when using high grade oil as feedstock (about 80% of the total production cost). The problems can be solved to a great extent by reducing the production cost (by using WCO as feedstock) and utilizing more efficient catalysts (heterogeneous solid catalysts with easy separation/removal after reaction). When comparing WCO-derived biodiesel with other biodiesels and conventional fuels, it becomes evident that it offers numerous advantages. These include reduced greenhouse gas emissions, enhanced engine efficiency, and decreased particulate matter emissions, all contributing to its appeal as an environmentally responsible energy source. WCO-based biodiesel stands out as a carbon-neutral fuel, emitting fewer pollutants and greenhouse gases than traditional diesel fuels. Notably, it can curtail CO_2 emissions by up to 78%, thanks to its closed carbon cycle during production. This underscores both the potential of WCO-derived biodiesel and the broader significance of biodiesel research in advancing sustainable energy solutions. Ongoing research will delve deeper into these performance comparisons, further establishing biodiesel's crucial role in the transition to greener and more sustainable energy alternatives.

NOMENCLATURE

WCO	Waste Cooking Oil
BTe	Billion Ton Equivalent
FFA	Free Fatty Acid
USA	United States of America
EU	European Union
RED	Renewable Energy Directive
RES-T	Transportation Sector
ILUC	Indirect Land Use Change
TPT	Third-Party Take-Back
BET	Biodiesel Enterprise Take-Back
WFO	Waste Frying Oil
UCO	Used Cooking Oil
UFO	Used Frying Oil
FAME	Fatty Acid Methyl Ester
DMC	Double-Metal Cyanide
MOR	Mordenite
BEA	Beta
FAU	Faujasite
MFI	ZSM-5
CN	Cetane Number

Elements and chemical symbol

Na	Sodium
CO_2	Carbon Dioxide
Al	Aluminum
Si	Silicon
OH-	Hydroxide Ion
H+	Hydrogen Ion (Proton)
H_2O	Water
KOH	Potassium Hydroxide
$C_3H_8O_3$	Glycerol
CH_3OH	Methanol
NaOH	Sodium Hydroxide
CH_3ONa	Sodium Methoxide
CH_3OK	Potassium Methoxide
H_3PO_4	Phosphoric Acid
H_2SO_4	Sulfuric Acid
BF_3	Boron Trifluoride
HCl	Hydrochloric Acid
CaO	Calcium Oxide
CH_3O^-	Methoxide Ion
ZnO	Zinc Oxide
Ca_2^+	Calcium Ion
O_2^-	Oxide Ion
$ZnO/Sr(NO_3)^2$	
MgAl-LDH	MgAl-Layered Double Hydroxide

Parameters utilized in equations

P_C	Critical Pressure
T_C	Critical Temperature

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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