ChemBioEng Reviews

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Waste Cooking Oil Conversion to Biodiesel Using Solid Bifunctional Catalysts

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Abstract

The draining of fossil fuels and their toxic influence on the environment has prompted the need for alternative fuels known as biofuels. Of the various types of biofuel, biodiesel has attracted wide interest in the world today since it promotes carbon neutrality. The transesterification and interesterification process remains the most widely used process route for biodiesel production. In this review, the performance efficiency of solid base, solid acid, and bifunctional solid acid-base catalysts for biodiesel production from waste cooking oil is considered. In particular, the benefit of exploring the biomass-derived acid-base heterogeneous bifunctional catalysts, current status, and future prospects for biodiesel production from waste cooking oil are elucidated.

Keywords: Acid-base bifunctional catalysts, Biodiesel, Biomass, Solid catalyst, Waste cooking oil

Received: August 01, 2022; *revised:* October 24, 2022; *accepted:* February 06, 2023

DOI: 10.1002/cben.202200036

1 Introduction

The urgent need for alternative sources of fuel aside from the ones obtained from the fossils is no longer news [1]. The pivotal purpose to be regarded as a driving force to seek substituent energy resources is the pollution of the environment [2]. Complicating the lingering energy crisis is the world's total primary energy consumption (TPEC) which reached over 150 000 000 GW h in 2015, and is projected to increase by 57 % up to 2050 [3]. Currently, 88 % of the mainly consumed energy is from fossils, of which about 90 % of this value is being used just in the transport sector [4]. This, in turn, draws about 60 % of the overall annual global consumed fuel [5].

Biofuel has been discovered to be a prospective alternative to fossil fuel in terms of eco-friendliness, improved combustion in automobile engines, and sustainability due to the availability of its feedstock [6]. Optimally, the consolidation of distinct characteristics such as diversity, biodegradability, low toxicity, lower content of sulfur, higher lubricating value, renewability, controllability, and accessibility has been associated with biofuel [7].

One of the major contributors to the global rise in carbon is a greenhouse gas known as carbon dioxide which is a result of anthropogenic activities [8]. It has been well thought out as the key contributor to climate change and global warming [9]. On the other hand, there is a significant reduction in the carbon dioxide emission in biodiesel due to the presence of sufficient oxygen [10–12]. It could also be noted that the nature of the emission of a biofuel depends on the nature of the feedstocks. Generally, biofuel feedstocks can be classified as primary and secondary sources of energy. The primary biofuel feedstocks can be defined as organic materials used in their natural unprocessed form, such as wood, dunghills, and animal dung fuel, which are used directly to produce electricity or heat while the secondary biofuels are the feedstocks indirectly derived from organic materials which may be plants or animals [13]. The secondary biofuel feedstocks can be further categorized into five subdivisions as shown in Tab. 1.

Biodiesel is a well-known biomass-based biofuel which is biodegradable with a lower toxic effect compared to petroleum-based diesel. It is sustainable and serves as a good substi-

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Table 1. Classification of secondary biofuel feedstocks [14].

Generations of feedstocks	Sources of feedstocks	Factors involved
First generation	Edible oil: sunflower oil, corn oil, palm oil, peanut oil, soya beans oil, cassava oil, and canola oil	– Fertilizer and water needed – Greenhouse gases are emitted – Not cost-effective – Food competition/increased food price – Land usage change
Second generation	Non-edible oil: jatropha oil, linseed oil, castor oil, Karanja oil, rubber oil	– Land and water usage – Fertilizer and pesticide usage – Greenhouse gases are emitted
Third generation	Waste-based oil	– No land and water usage – Sustainable – Low-cost feedstock – No food competition – Cleaner environment
Fourth generation	Algal-based oil	– No greenhouse gases are emitted – High oil yield – Fertilizer needed – No food competition – High cost
Fifth generation	Genetically engineered crop	– No greenhouse gases are emitted – High oil yield – Food competition is eradicated – Sustainable

tute for conventional diesel [15]. Biodiesel is produced from fats and oils (soybean oil or waste cooking oil) chemically or biochemically. It is an oil consisting of long-chain alkyl-esters or mono-alkyl esters of long-chain fatty acids obtained from the reaction of oils or animal fats with alcohol [16]. The scheme in Fig. 1 displays a structural representation of the molecules of biodiesel. It is often a long chain of carbon atoms with attached hydrogen atoms and then at one end with the alkanoate functional group. Biodiesel comprises long-chain fatty acid methyl esters (FAMEs) which have proficient combustion characteristics due to the occurrence of appreciable higher oxygen content and higher flash point [17].

Waste cooking oil (WCO) as illustrated in Fig. 2 is an important highly available bioresource from oils such as sunflower oil, palm oil, and coconut oil. WCOs are oils that have been used several times for cooking or frying and cannot be further employed for their main purpose [18]. It is a fatty waste feedstock which is not good for human consumption. It contains water and high free fatty acids (FFAs).

Generally, WCO comprises about 36.92 % and 63.08 % of saturated and unsaturated fatty acids, respectively, as depicted in Fig. 3. So, before it is utilized for quality biodiesel production, usually WCO undergoes pretreatment or post-treatment. Of course, this increases the cost of production.

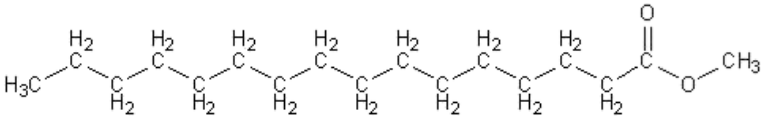


Figure 1. Structural representation of biodiesel.



Figure 2. Waste cooking oil.

The quality of biodiesel could also be affected by other factors such as the oxidation process, the nature of feedstocks, and catalyst type. The oxidation parameter is usually attributed to the double bonds in the skeleton of the fatty acid molecules of feedstock [20]. Feedstocks like jatropha oil, castor oil, and WCO are cheaper sources of oil but are low-graded due to high FFAs which could affect the quality of biodiesel. Lastly, the catalysts with a weak or unstable site could also influence the quality and performance of the biodiesel produced as an active site with required chemical properties which are needed for good features [21]. Therefore, homogeneous (acid or base) and heterogeneous (acid or base) catalysts have been utilized to improve the quality of biodiesel [22].

The homogeneous catalysis of WCO into biodiesel requires pretreatment and post-treatment

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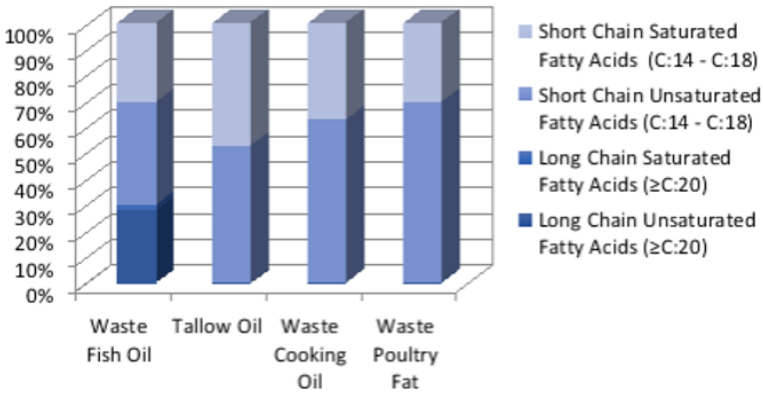


Figure 3. Saturated and unsaturated fatty acids.

steps which lead to higher cost of production. On the other hand, heterogeneous catalysis of WCO for biodiesel production tends to give a better result when compared with the former. However, the challenge remains in the formation of soap and water for solid base catalysis, while high catalyst amount, reaction time, and lower acidic site for solid acid catalysis tend to incur more cost of production [23]. Hence, to solve this challenge, researchers employed biomass-derived bifunctional catalysts comprising both solid acid and base catalysts due to their complementing advantages.

Although there have been numerous researches on the use of low-grade feedstocks along with stable catalysts, there exist limited studies on the use of biomass-derived bifunctional catalysts in the production of biodiesel from low-grade feedstocks like WCO. Therefore, this review focused on the discussion of methods of converting WCO to biodiesel, different types of acid/base of heterogeneous catalysts, and their roles in the conversion of WCO to biodiesel with the current status and future prospects. The benefits of exploring biomass-derived heterogeneous bifunctional catalysts for biodiesel production are also discussed.

2 Biodiesel Production

The production involves the conversion of oils or fats to biodiesel [24]. This conversion could be achieved through various routes such as microemulsion (mixtures of surfactant, oil cosurfactants, and water), blending/dilution (biodiesel mixed in different concentrations such as B5 and B20), pyrolysis (thermochemical conversion of biomass in the absence of oxygen at a high temperature depending on the feedstocks), transesterification reaction (reaction between oil or fat with methanol or ethanol), supercritical fluids (mixture above its critical pressure and temperature but below the pressure required to condense into a solid), and interesterification reaction (reaction between oil or fats with methyl acetate or dimethyl carbonate to biodiesel and triacetin). These methods have been reported to convert WCO to biodiesel [25].

2.1 Methods of Conversion of Waste Cooking Oil to Biodiesel

The conventional methods of biodiesel production have been utilized with WCO. For instance, Trabelsi et al. [26] did the pyrolysis of WCO using a laboratory 15-scale fixed-bed reactor and obtained a maximum bio-oil yield of 80 wt % at 800 °C and 15 °C min^{-1} heating rate. The bio-oil fuel properties revealed that this pyrolytic oil has a high caloric value (8843 kg $kcal^{-1}$) but some other properties still need to be improved. Also, the operating condition of the system seems very high which consequently requires higher energy consumption.

Wan-Mahari et al. [27] carried out the microwave co-pyrolysis of waste-polyolefin (WP)/WCO at different ratios under N_2 atmosphere and vacuum environment for 20 min. The yield's peak of the liquid oil was 62 wt %, which was obtained at a WP/WCO ratio of 2:1 under a vacuum environment. The oil obtained shows valuable properties which could be applied to fuel combustion engines.

French et al. [28] demonstrated that bio-oils produced through pyrolysis could function as fuel for constant power production using turbines or boilers but yet require significant modification for usage as a transportation fuel. Bora et al. [29] reported that the production of biodiesel from WCO is associated with some deficits such as poor cold flow properties and low oxidation stability. Thermogravimetric methods were used to access cold flow properties and ignition delay and were improved by the formation of water-in-biodiesel microemulsions by applying various surfactants. It was found that Span 80-based microemulsion experienced precipitation during its storage for 60 days. The total fatty acid methyl ester content in purified biodiesel was notably increased from 90.2 % to 96.3 %, with an improvement in its oxidation stability properties.

Bora et al. [29] also documented biodiesel from WCO using microemulsion by hybridization biofuel as a substitute for fossil diesel. The microemulsion-based hybrid biofuel systems were contrived using ethanol as a dispersed phase and exhibited fuel properties which measured up to American Standards for Testing and Materials (ASTM D6751). They also emphasized the preparation of a simple biofuel system by micro-emulsification without using any externally added surfactant. Excellent physical stability was exhibited by simple fuel systems formulated only by using butan-2-ol as a co-surfactant.

Nigatu and Marchetti [30] stated that the proper composition of biodiesel microemulsion includes oil, fossils diesel, cetane improver, surfactant, and alcohol. Phasukarratchai [31] also reported the phase behavior and biofuel properties of waste cooking oil-alcohol-diesel blend in microemulsion form and found that no surfactant is required for a homogeneous phase blend when butanol is blended with WCO-diesel fuel blend (WDF), unlike WDF with ethanol. It was also found that the phase behavior of WDF-ethanol blends with hydrophobic surfactants was more satisfactory than WDF-ethanol blends with more hydrophilic surfactants. They concluded that the kinematic viscosity of WDF blends is a function of surfactant and its hydrophile-lipophile balance (HLB) value.

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The transesterification reaction of WCO is the most broadly used route for biodiesel production [32]. The reaction involves the alteration of triglycerides to methyl esters supported by a catalyst. Although, the transesterification reaction is sensitive to high FFAs in low-grade feedstocks like WCO, however, the reaction could be improved by synthesizing heterogeneous catalysts with desired physical and chemical properties needed to simultaneously reduce the high FFAs and transesterify the triglycerides in a one-step transesterification process [14] or through a two-step transesterification process. For instance, Kadapure et al. [33] reported biodiesel synthesis from WCO using a two-step transesterification process. Alcoholysis was carried out to examine the effects of temperature, reaction time, catalyst dosage, and the methanol/WCO ratio on the yield of biodiesel. The biodiesel yield of 70 % was attained for WCO at an oil/methanol ratio of 1:8, 60 °C temperature, time 4 h using calcium oxide as catalyst. It was concluded that WCO is a prominent feedstock for biodiesel production.

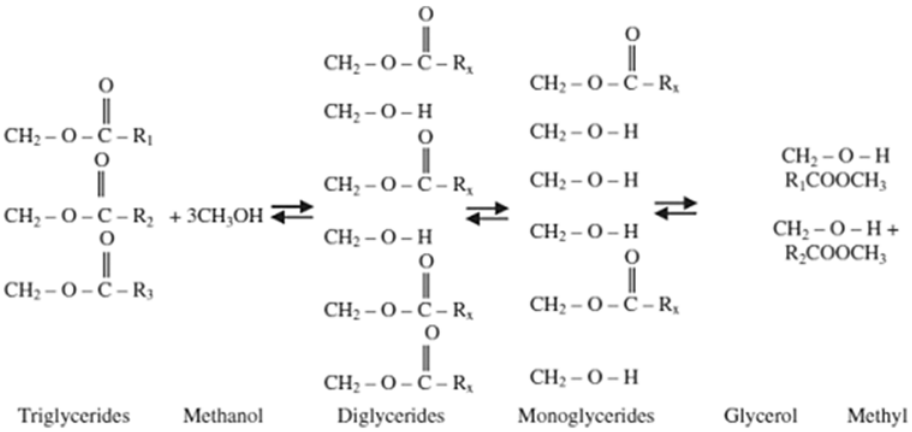


Figure 4. Transesterification of waste cooking oil.

As illustrated in Fig. 4, transesterification requires reacting methanol or lower hydrocarbon chain alcohols with the WCO [34]. Chemical compositions and physical properties of WCO which consequently may affect the quality of biodiesel conversion are given in Tab. 2.

Costarrosa et al. [38] reported the transesterification of WCO using methanol as a reactant and calcined Mg-Al hydrotalcite as a solid catalyst. With Box-Behnken design, the FAME content (86.23 %) was predicted with an R^2 value of 0.9845. Moreover, preliminary studies using commercial SrO as a catalyst for WCO transesterification in a continuous-flow reactor were reported by Tangy et al. [39]. A high value of 99.2 wt % conversions of WCO into biodiesel was achieved. Putra et al. [40] transesterified WCO with methanol using CaO/SiO_2 as a catalyst. When CaO was used alone, the yield of biodiesel was 78 % but when supported with peat clay the yield increased to 91 %. This is due to the enlargement of the CaO surface area.

Hence, the transesterification route has been shown to be efficient for the conversion of WCO to biodiesel. However, the high FFA content of WCO still poses challenges for its wider applicability. The two-step transesterification reaction has been proven to achieve better results although it tends to increase the cost of production. Another viable approach could be the modification of catalysts into the desired physical and chemical properties for reducing high FFAs in a single-step WCO transesterification process.

Table 2. Physicochemical properties of waste cooking oil [35–37].

Chemical composition		Physical parameters	
Fatty acids	*Range*	*Parameters*	*Range*
Palmitic acid [wt %]	8.1–8.5	Density [kg m^{-3}]	800–920
Oleic acid [wt %]	6.1–21.2	Kinematic viscosity at 40 °C [mm^2s^{-1}]	34–35
Linolenic acid [wt %]	1.7–5.9	Iodine number [g iodine kg^{-1}]	430–1080
Caproic acid [wt %]	1.6–1.8	Acid value [g KOH kg^{-1}]	0.67–30.0
Caprylic acid [wt %]	9.1–9.5	Saponification value [g KOH kg^{-1}]	180–200
Capric acid [wt %]	8.9–9.2	Sodium content [mg kg^{-1}]	4.1–7.9
Linoleic acid [wt %]	50–58.9	Peroxide [mg kg^{-1}]	5.0–23.1
Stearic acid [wt %]	1.6–3.1	Sulfur content [mg kg^{-1}]	0.02–4.00
		Others	4.2
		Ash	0.030
		Water content	0.25–1.9

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3 Need for Conversion of Waste Cooking Oil to Biodiesel

To justify the use of WCO as a potential starting material for biodiesel production, researchers have reported on the environmental deficiency of WCO. Lam et al. [98] stated that there have been challenges arising from the huge production of WCO due to the activities of catering, commercials, and households [41]. For example, discarding used cooking oil through kitchen sinks may lead to the creation of obstacles to flow in the conduit when they solidify. Oils disposed carelessly find their ways into the water bodies, which consequently increases the biological oxygen demand, thereby reducing the oxygen required by the aquatics and increasing pollution. When cooking oil is repeatedly exposed to high heat above 300 °C for an elongated time, it leads to the generation of unsafe compounds like lipid peroxidation products. A high risk of developing hypertension, atherosclerosis, carcinogenesis, and low-density lipoprotein (LDL) levels is associated with the use of WCO due to the presence of surplus polar compounds [42]. Hence, it is necessary to find other applications for the waste oils to allay their negative effect on the surroundings and human health.

In Tunisia, it was estimated that the annual consumption of vegetable oil reaches about 4017 kg per person in a year. According to the Energy Information Administration USA and the European Union, the annual production of WCO mounts up to about 378 000 m^3 and 700 000 000 to 341 000 000 000 kg per year, respectively [43]. But, WCO in diesel engines could result in poor combustion emissions, clogging, smoking, and- environmental hazard [44]. Also. Suresh et al. [45] reported that at a very high temperature during the combustion process the WCO-biodiesel produces a high amount of NOx. Fig. 5 shows the percentage NOx in WCO as compared with other feedstocks.

It has been reported that to reduce the poor emission characteristics, WCO could be efficiently reused by the addition of *n*-propanol. Also, an adequate conversion of WCO to biofuel such as biodiesel by using a well-modified bio-based acid-base bifunctional catalyst could be a better option. This catalyst could simultaneously reduce the high FFAs and transesterify triglycerides in WCO. WCO will become very admissible mostly in developing countries since it will help to eliminate the fear of competition of the feedstock with food.

3.1 Pretreatment of Waste Cooking Oil

Usually, WCO contains high FFAs, high water content, and solid particles. These compositions often hinder the quality and quantity of biodiesel that is produced. To address this challenge, researchers introduced the treatment of WCO before the actual biodiesel production. Generally, the pretreatment of WCO can be divided into two major parts: physical methods (membrane separation/filtering, adsorption, extraction with solvent and distillation) and chemical methods (esterification and neutralization) [47].

Casallas et al. [48] reported optimization proceedings for the pretreatment of WCO collected from food restaurants by filtering with a cellulose filter, drying with silica gel (as adsorbents), and esterifying to transform the high FFAs to methyl esters using sulfuric acid. It was concluded that the optimal conditions for WCO pretreatment were 60 °C, 1 wt % sulfuric acid with 4:1 alcohol:oil molar ratio in 2 h. After pretreatment of WCO, the moisture content was less than 1 %, solids suspended was 0.25 %, and the acid value was found to be 1.38 mg KOH g^{-1}. Falowo et al. [49] also reported the pretreatment of WCO before biodiesel production. They stated that the high FFA content of the WCO was reduced from 5 to 1 mg KOH g^{-1} with H_2SO_4 as a catalyst in an esterification reaction.

Recently, due to high cost and separation problems, pretreatment of WCO has been performed through the adsorption process. Schneider et al. [50] reported the pretreatment of WCO by the adsorption process. Results from the use of activated carbon, rice husk, and agro-industrial waste adsorbents were compared. It was concluded that using the activated carbon, a 63 % reduction of FFAs was achieved at a temperature of 22.4 °C, 169.64 rpm, and 3.39 g of adsorbent. Similarly, 63 % of FFAs was achieved using the rice husk at a temperature of 22.4 °C, 80.36 rpm, and 1.61 g of adsorbent.

Another approach to reduce the cost of the pretreatment of WCO (especially through esterification reaction) is to develop catalysts that possess both physical and chemical properties which could simultaneously esterify and transesterify the WCO to biodiesel. Li et al. [51] documented the simultaneous esterification and transesterification of WCO without pretreatment using a solid acid catalyst derived from the sulfonation of pyrolyzed rice husk. The FFA conversion reached 98.17 % after 3 h, while the yield of FAME was 87.57 % after 15 h. It was concluded that the catalyst has the potential to simultaneously esterify and transesterify WCO with high FFA content. Although, solid acid catalysts have good potential in reducing the FFA content of WCO, however, the rate of reaction is relatively slow. Hence, researchers' attention has also been drawn towards the use of solid bifunctional catalysts that possess the properties to simultaneously esterify and transesterify WCO to biodiesel and could also increase the rate of reaction.

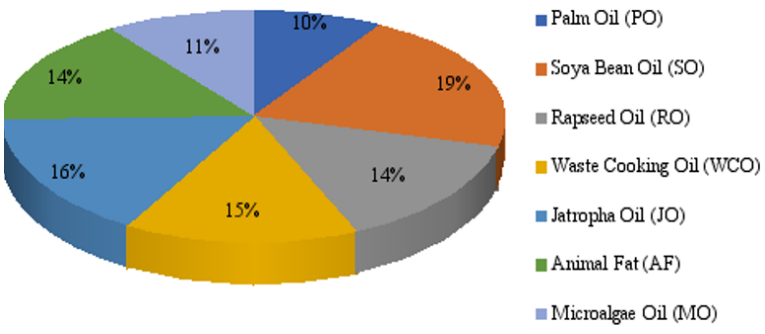


Figure 5. Percentage NOx in WCO compared with other feedstocks.

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3.2 Advantages of Using Waste Cooking Oil: Cost Perspectives

The overall cost of biodiesel production usually depends on feedstock type, catalyst type, and pretreatment cost. Research by Al-sakkari et al. [52] showed that the cost of biodiesel production mostly depends on the feedstock type. They reported the comparative techno-economic analysis of using WCO and virgin soybean oil. The sensitivity analysis revealed that the level of profit in the production of biodiesel highly depends on the feedstock price. It was further recommended that shifting towards WCOs would enhance a feasible and economic process. Moreover, El-Gharabawy [53] concluded from the study on the cost analysis for biodiesel production from WCO in Egypt that biodiesel production would yield a good income due to the low cost of WCO. This result was based on an experimental design with a biodiesel yield of 99.9 % under optimum conditions.

On the contrary, Yanbin et al. [54] stated that the total cost of producing biodiesel from WCO is 63 % higher than fossil diesel and that although WCO is commercially cheap, however, the relatively high pretreatment cost accounts for 15.06 % of the 63 % production cost. It was then concluded that a special waste management policy should be implemented and WCO recycling technology should be enhanced to make WCO biodiesel more economically feasible. In another study, Karmee et al. [55] also performed research on the techno-economic evaluation of biodiesel production from WCO using Hong Kong as a case study. It was stated that out of the three different catalysts (acid, base, and lipase) evaluated for WCO to biodiesel production, the acid catalyst was found to be cheaper compared to the other catalysts examined. It was concluded that the catalyst type could also affect the cost of WCO biodiesel.

However, the advantage of using WCO has been documented to have less effect on arable land – its use, cheaper, and a sustainable feedstock for biodiesel production from the cost perspective would be more profound if waste management policies are implemented. The government could put into operation policies for proper WCO has been documented to have less effect on arable land – use, cheaper and a sustainable feedstock disposal as this would reduce the pretreatment steps and consequently the cost of pretreatment before biodiesel production. These policies could align with the environmental policies of circular bioeconomy, zero-discharge principles, and the united nation sustainable development goals [56]. Based on catalysis, an alternative to reduce the cost of production of biodiesel from WCO has been documented to have less effect on arable land – use, cheaper and a sustainable feedstock could be to develop green catalysts with inherent chemical properties for simultaneous pretreatment and conversion of WCO has been documented to have less effect on arable land – use, cheaper and a sustainable feedstock to biodiesel.

3.3 Current Status of Conversion of Waste Cooking Oil to Biodiesel

In recent times, researchers tend to shift attention toward the interesterification of triglycerides with acyl acceptors such as dimethyl carbonate, methyl acetate, and ethyl acetate to produce a glycerol-free biodiesel or glycerol-blended biodiesel (biodiesel-like-biofuel). This strategy has been introduced to avoid the process of separating glycerol from the biodiesel produced since glycerol tends to pose a significant obstacle to the high yield of biodiesel. This process inclines to incorporate the glycerin or glycerol with the produced biodiesel thereby making it miscible with FAMEs.

The key difference between the traditional biodiesel produced from triglycerides with methanol and triglycerides with other acyl acceptors is the presence of glycerol derivatives molecules miscible in the FAMEs products. In this way the unique transesterification process (interesterification) allows the highest atom efficiency, leading to the total conservation of the oil or fats into any of the biofuels known as gliperol, eco-diesel or dimethyl carbonate-biodiesel [57]. This means that the reactant used remains in the product formed and is also directly used as biofuel.

Presently, many processes in interesterification reactions employ enzymes as a catalyst, however, limited work has been documented on the use of biomass-derived heterogeneous bifunctional catalysts in WCO has been documented to have less effect on arable land – use, cheaper and a sustainable feedstock interesterification. Fig. 6 demonstrates the interesterification reaction between WCO and dimethyl carbonate to give gliperol (biodiesel-like- biofuel).

Gharat and Rathod [58] reported an interesterification reaction between WCO and dimethyl carbonate (DMC), hich is a substitute for methanol, to produce eco-diesel or DMC-diesel in the presence of an immobilized enzyme catalyst (Novozym 435) under the influence of ultrasound irradiation. The effect of the operating parameters such as temperature, the ratio of oil:dimethyl carbonate, speed of agitation, and enzyme loading on the FAME conversion was investigated. The maximum yield of 86.61 % was achieved at a reaction time of 4 h, 10 % catalyst loading, temperature 60 °C, and DMC:oil ratio of 6:1 by ultrasonic irradiation coupled with stirring.

Ganesh et al. [59] also reported an interesterification in the synthesis of biodiesel from WCO in a hydrodynamic cavitation reactor. The highest yield of biodiesel (90 %) was achieved using a molar ratio of oil to methyl acetate being 1:12, inflow pressure of 3 bar, and catalyst loading of 1.0 %. It was stated that WCO has been documented to have less effect on arable land – use, cheaper and a sustainable feedstock could be a prospective feedstock in interesterification reactions toward the production of good-quality glycerol-blended biodiesel biofuel in the future. Therefore, transesterification or interesterification of WCO could give a better quantity and quality of biodiesel which would be compatible with most combustion engines. Also, to promote the sustainability of the environment and the commercialization of biodiesel, the process could be used together with biomass-derived heterogeneous catalysts.

Currently, heterogeneous bifunctional catalysts resulting from biomass waste have received further attention [22]. This type of catalyst offers several advantages which include reusability, improvement of soil carbon content when disposed, renewability, availability, great stability, nontoxicity, lofty catalytic activity, in both acidic and basic circumstances and elevated water forbearance properties [60] which depend on the

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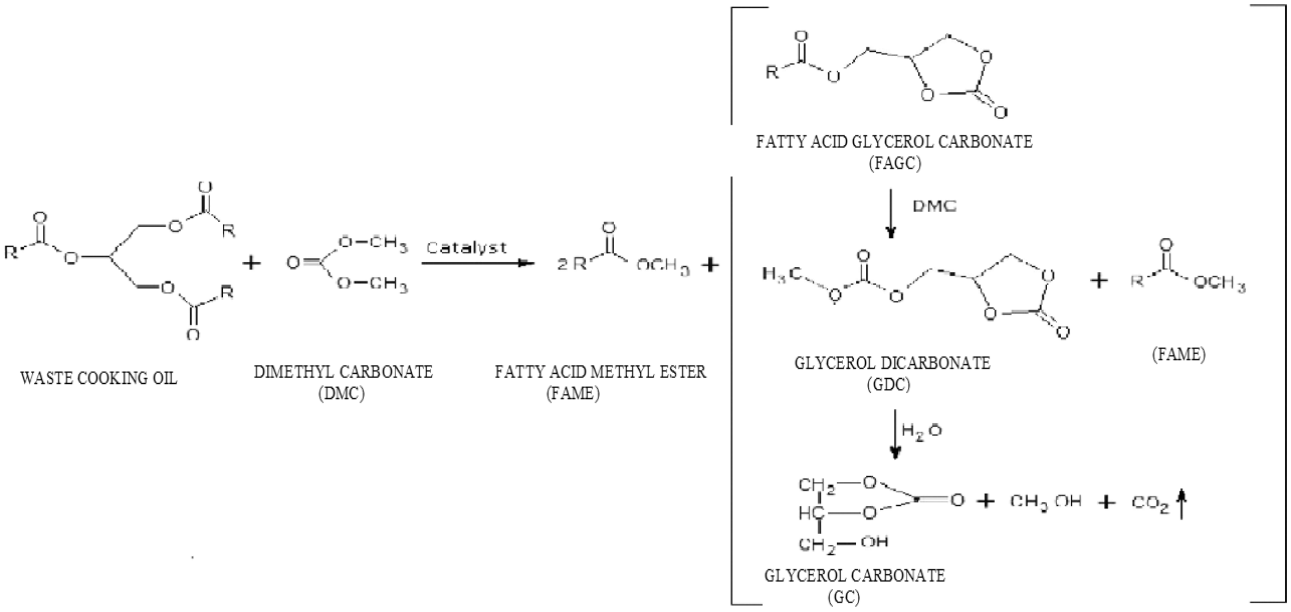


Figure 6. Interesterification reactions between WCO and dimethyl carbonate.

quality and strengths of active acid or basic sites. For future research, the exploitation of biomass-waste oil and biomass-waste heterogeneous catalysts for biodiesel production may be a better option as it eradicates problems encountered during homogeneous operations and it reduces cost [61].

Unlike homogeneous catalysts, heterogeneous catalysts are reusable and easily separated from the products, thus minimizing the cost of synthesizing catalysts over time for the same production process. Also, the use of waste biomass as solid bifunctional catalysts could contribute to a waste management scheme, mitigate the cost of commercially available catalysts, and also extend the production of biodiesel all over the world [62]. It is worth noting that extra development and survey of better biomass-derived acid-base bifunctional catalysts are necessary on the way to improve catalytic performance such as low leaching capability of the active sites for the production of biodiesel from WCO [63].

3.4 Advantages and Disadvantages of Different Processes Used in the Conversion of Waste Cooking Oil to Biodiesel

The merits and demerits of several methods used in the conversion of WCO to biodiesel are highlighted in Tab. 3. Out of all the methods, transesterification has shown to be highly prospective although it possesses some drawbacks, too. If interesterification, which is a method of transesterification, is properly managed, it could be the future process of conversion of WCO to biodiesel.

4 Role of Acid Heterogeneous Catalysts in the Transesterification Reaction of Waste Cooking Oil to Biodiesel

WCO is usually characterized by a very high FFA content between 0 and 40 % depending on the cycle of usage, therefore, an acid site that will inhibit the formation of soap by reducing the FFAs drastically is required. Acid heterogeneous catalysts could perform both transesterifications of triglycerides (TGs) and esterification reactions of FFAs. Acid heterogeneous catalysts can be effectively synthesized from the sulfonation of carbon-based material.

Shu et al. [67] produced biodiesel from WCO with sufficient amounts of FFAs using a carbon-based solid acid catalyst as a heterogeneous acid catalyst. The carbon-based solid acid catalyst was prepared by carbonizing the waste vegetable oil asphalt and then sulfonated. Results showed that on using a methanol:oil ratio of 16.8:1 and 0.2 wt % of catalyst (relative to oil), the maximum conversion of triglycerides and FFAs reached 80.5 wt % and 94.8 wt% after 4.5 h at 220 °C.

Wang et al. [68] also documented a magnetic solid acid catalyst in the form of sulfamic-acid- and sulfonic-acid-functionalized silica-coated crystalline Fe/Fe_3O_4 core-shell magnetic nanoparticles (MNPs). Of the catalysts used in the conversion of WCO, the sulfamic-acid-functionalized MNPs proved to be more proficient and reliable after five cycles of use. Also, the catalyst recovery was efficient due to the magnetic effect [68]. Tab. 4 presents various acid heterogeneous catalysts that have been used in the conversion of WCO.

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Table 3. Advantages and disadvantages of methods of conversion of waste cooking oil to biodiesel.

Methods of conversion	Advantages	Disadvantages
Microemulsion	– Adds a good spray feature to the biodiesel – Higher alkanol molecules can be used unlike alcoholysis – Little or no energy is required – Very low temperature	– Causes the injector needle to stick – Incomplete combustion – Formation of carbon deposit
Blending/dilution	– Little or no energy is required – No catalyst is required – Very low temperature	– Corrosiveness from acid molecules – Gum formation – Thickening of lubricating oil – Storage problems – Deterioration of oil – Formation of carbon deposit
Pyrolysis	– A fast reaction is obtainable if fast pyrolysis is done – Low cost of production – The process is simple and ease – Less waste is produced	– High ash content in products – Deposition of carbon content – Insupportable cloud and pour point – Much energy is required
Transesterification	– The process is cheaper – It is simple – Good storage properties – No carbon deposition – Good physicochemical properties of biodiesel produced	– Synthesis of catalyst – Separation of product from the catalyst used – Contamination of product may occur – Presence of NO_2 in the product – Formation of side products
Supercritical fluids	– Requires a short time – No catalyst is required – Recovery of glycerol is easier	– High operating cost – High temperatures and pressure are required
Interesterification	– The process is cheaper – It is simple – No side products – Higher biodiesel yield – Good storage properties – No carbon deposition – Good physicochemical properties of biodiesel produced	– Synthesis of catalyst – Separation of product from the catalyst used – Contamination of product is minimal

Table 4. Acid heterogeneous catalysts for waste cooking oil transesterification.

Catalysts	Time [h]	Methanol: oil	Temp. [°C]	Catalyst loading [wt %]	Reusability	Feedstock	FFA [%]	FAME yields [%]	Ref.
Carbonized and sulfated asphalt	4.5	16.8:1	220	0.2	5 cycles	WCO	–	89.9	[69]
SO_4^{2-}/SnO_2-ZrO_2	1	20:1	170	3.0	5 cycles	WCO	10.0	86	[70]
$Al(HSO_4)_3$	0.83	16:1	220	0.5	3 cycles	WCO	–	81	[71]
Silica-sulfuric acid	0.5	6:1	60	1.5	5 cycles	WCO	2.0	90	[72]

5 Role of Base Heterogeneous Catalysts in the Transesterification Reaction of Waste Cooking Oil to Biodiesel

Base heterogeneous catalysts are faster and have higher activity than acid catalysts [73]. Just like solid acid catalysts, their reusability and recoverability are significant [74]. They are corrosion-free and exhibit mild reaction conditions. Base heterogeneous catalysts can be classified as mineral and biomass catalysts. The minerals include calcium oxide (CaO), strontium oxide (SrO), zinc oxide (ZnO), and Na/SiO_2 whereas biomass catalysts include CaO which can be obtained from different sources like scallop shell, mussel shell, chicken eggshell, *Chicoreus brunneus* shell [75], waste chicken eggshells, and mollusks.

Birla et al. [76] reported the synthesis of high-yield biodiesel from waste frying oil using a heterogeneous base catalyst derived from a snail shell. However, they have higher reaction conditions and saponification as a side reaction [77]. Farooq

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et al. [78] produced biodiesel from WCO using a heterogeneous base catalyst derived from chicken bones. The washed bones were dried in ovens at 110 °C for about 6 h and then ground to powder. The powdered material was calcined in the furnace at 800 °C, 900 °C, and 1000 °C for 4 h. Among all the catalysts used, the powdered material at 900 °C shows high catalytic activity in the biodiesel production from WCO under the optimized reaction conditions of a methanol:oil molar ratio of 15:1, a reaction time of 4 h, reaction temperature of 65 °C, catalyst loading of 5 wt %, and 500 rpm agitation speed which in turn gave a biodiesel yield of 86.33 %.

Furthermore, Chakraborty et al. [79] reported calcined washed Rohu fish scale (*Labeorohita*) as a heterogeneous base catalyst with a maximum biodiesel yield of 97.73 % at optimal parameters of 997.42 °C calcination temperature, oil:methanol molar ratio 1:6.27, and catalyst loading of 1.01 wt % of oil. The combination of organic and inorganic materials that have been used for biodiesel production includes calcined goat bone treated with potassium hydroxide (KOH) [80] and empty fruit bunch (EFB) ash doped with KOH [81]. These base catalysts produced also good results. However, these yields could be improved if the catalyst is optimally modified with acid catalysts from a biomass-based source to form a bifunctional catalyst. This can prospectively improve the catalyst's chemical properties thereby reducing soap formation during the transesterification reaction and decreasing the overall production cost. Tab. 5 presents various base heterogeneous catalysts that have been utilized in the transesterification of WCO.

6 Role of Acid-Base Bifunctional Heterogeneous Catalyst in the Transesterification Reaction of Waste Cooking Oil to Biodiesel

In alcoholysis reactions, base heterogeneous catalysts have higher reaction rates than heterogeneous acid catalysts, whereas acid heterogeneous catalysts could withstand high FFAs in WCO [89]. A base catalyst could cause the formation of soap whereas an acid catalyst inhibits the production of soap by reducing the FFA content [90]. Hence, to overcome these distinct challenges associated with each catalyst type, the development of biomass-based heterogeneous bifunctional catalysts by synergizing both the acid sites and basic sites could be a solution. Bifunctional catalysts such as $CaO\text{-}La_2O_3$, $CaOFe_2O_4\text{-}Ca_2Fe_2O_5$., $La_2O_3\text{-}ZnO$, and $La_2O_3\text{-}Al_2\text{-}O_3$ [87] have been utilized and provided a very good performance. This is because they possess high surface area, pore volumes, adequate morphological structures, and stable active sites that can promote both esterification and transesterification reactions in a single-step process. However, these materials remain expensive compared to bio-sourced materials [91]. Fig. 7 illustrates the general reaction mechanism for a bifunctional catalyst.

There are five steps required for a complete mechanism in biodiesel production through acid-base bifunctional catalysis. These steps are repeated for the production of each molecule of the FAMEs. In the first step, the reactants, triglycerides (WCO) and alkanol (methanol) diffuse from the bulk solution into the active site (acidic and basic site) of the bio-derived bifunctional catalyst. Secondly, the FFA carbonyl group gets adsorbed at the acidic site (represented with a sphere) on the catalyst for the esterification reaction (or pretreatment process) to occur while the molecules of the methanol get adsorbed on the basic site (represented with a star) for transesterification reaction to occur. This situation allows for the carbonium ion (positively charged carbon) and the oxygen anion, respectively.

In the third step, there is a surface reaction in that for both the acidic and basic active sites there is a nucleophilic hit on the esters by the methanol (CH_3O–H) molecules. This hit leads to the formation of a tetrahedral intermediate. In the fourth step, one molecule of FAMEs and one molecule of water (H–O–H) on the acidic site are revealed due to the distraction of the hydroxyl group from the tetrahedral intermediate. Furthermore, the C–O bond splits to form one molecule of FAMEs

Table 5. Base heterogeneous catalysts for waste cooking oil transesterification.

Catalysts	Time [h]	Methanol: oil	Temp. [°C]	Catalyst loading [wt %]	Reusability	Feedstock	FFA [%]	FAME yields [%]	Ref.
CaO (chicken eggshell)	11	6:1	–	5.8	5 cycles	WCO	1.80	97	[82]
CaO (scallop shell)	2	6:1	65	5	5 cycles	WCO	0.62	86	[83]
CaO (mussel shell)	–	24:1	–	12	5 cycles	WCO	–	94.1	[84]
CaO (bivalve clamshell)	3	18:1	65	8	–	WCO	1.12	95.84	[85]
CaO (chicken manure)	–	15:1	65	8	4 cycles	WCO	1.00	> 90	[86]
CaO (*Chicoreus brunneus* shell)	2	30:1	65	0.4	7 cycles	WCO	0.61	93	[87]
SrO	–	12:1	65	–	10 cycles	WCO	–	99.2	[39]
$CaAl_2$-CLDH (hydrocalumite)	5	< 6:1	65	5	4 cycles	WCO	1.80	> 90	[88]
Calcined snail shell (CaO)	8	6.03:1	65	2	–	WCO	0.97	87.28	[76]

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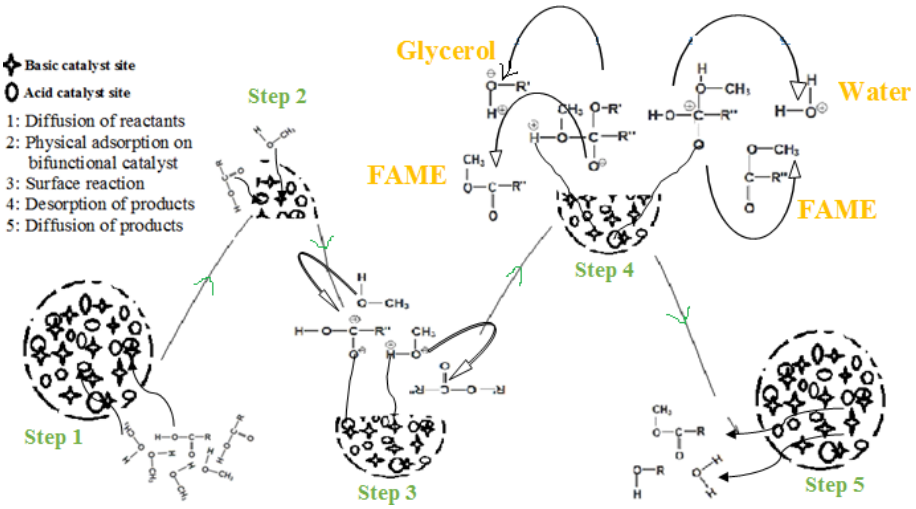


Figure 7. Mechanism of reaction for the production of biodiesel using bifunctional catalysts.

and glycerol as other products. Finally, the products get desorbed from the active site of the catalyst and then diffuse back into the bulk solution [92, 93].

The bifunctional heterogeneous catalyst with the acid-base site has drawn much attention over the past decades. They are solid catalysts capable of carrying both transesterification of TGs and esterification of FFAs without being affected by the water content and could result in reduced cost of production. Bifunctional heterogeneous catalysts are highly prospective in that they can be easily modified to take account of desired catalytic properties so that the inhibition of the formation of FFAs will be effective.

Researchers have made numerous attempts to improve the catalytic activity of the bifunctional catalysts since one of the major challenges facing this catalyst is the deactivation of the active sites by leaching after a few numbers of usages, thereby reducing its chemical reactivity and reusability [94]. The reusability property contributes vastly to the cost of producing biodiesel and its marketability [95]. For instance, Macario et al. [96] transesterified waste oilseed fruits and methanol using K-ITQ-6 (K means potassium) loaded on delaminated zeolite (ITQ-6) by ionic exchange as a bifunctional catalyst. During the reusability studies, the deactivation of the catalyst occurred significantly due to the leaching out of potassium after the first cycle. The biodiesel yield decreased from 87 % to 35 % after the second cycle. Therefore, it is worth noting that a small number of cycles could increase the cost of production since more catalysts will be added for replacement [97].

The kinetics of heterogeneous bifunctional catalysts for biodiesel production has been studied [98]. However, limited work has reported the transesterification of WCO using biomass-based heterogeneous bifunctional catalysts as this may aid to improve the sustainable process of catalyst development and lower the costs of production. Aderibigbe et al. [99] documented the kinetic study of WCO using biomass-derived bifunctional heterogeneous catalysts (sulfonated corncob/activated cow bone) in biodiesel synthesis, stating that the reaction follows a pseudo-first-order kinetics model with an activation energy of 21.4883 kJ mol^{-1}.

Further research would be needed to decrease the activation energy of the reaction via the modification of novel acid-base catalysts from biomass sources with stable active sites and improved sustainable procedures for its development. Although some researchers have been able to exploit the benefit of using biomass-derived acid-base bifunctional catalysts, however, more studies focus on reducing the costs of production, improving the reaction temperature and reaction time, and commercialization and waste management schemes are still needed. Tab. 6 lists some of the explored bifunctional catalysts for WCO and their results.

Table 6. Acid-base heterogeneous catalysts for waste cooking oil transesterification.

Catalysts	Time [h]	MeOH: oil	Temp. [°C]	Catalyst loading [wt %]	Reusability	Feedstock	FFA [%]	FAME yields [%]	Ref.
[CTA] MCM-41	3	80	0.1	5 cycles	8:1	WCO	1.10	93.0	[100]
Tungsten-loaded CaO/hydroxy-apatite	5	100	10	4 cycles	6:1	WCO	12.19	98.9	[101]
Mo/γ-Al_2O_3-MgO	5	100	5	10 cycles	27:1	WCO	–	91.4	[102]
$Fe_2O_3MnOSO_4^{2-}/ZrO_2$	4	180	3	7 cycles	20:1	WCO	17.5	96.5	[103]
Quintinite-3T	2	70	10	5 cycles	12:1	WCO	15.0	96.0	[104]
K-ITQ-6/KOH	24	180	5	2 cycles	20:1	WCO	6.08	79.7	[105]

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7 Brief Comparison of Acid, Base, and Acid-Base Bifunctional Heterogeneous Catalysts in Waste Cooking Oil Conversion to Biodiesel

The advantageous property of the synergetic effect of acid and base bifunctional catalysts allows for the mitigation of disadvantageous properties of the acid catalysts and base catalysts when considered individually [106]. The bifunctional catalyst may show more durable and reusable properties if considered for further research based on strategic modifications and optimization of its components. The leaching of the active site can be extremely mitigated by allowing the active site to be strongly bonded to the precursors. The advancement remains in developing biomass-based bifunctional catalysts, not just for cost consideration but also for the sustainability of resources used in biodiesel production. Tab. 7 gives a summary of the advantages and disadvantages of the acid, base, and acid-base bifunctional catalysts.

8 Future Prospects

There has been a shift from mineral sources to biomass-based resources required for biodiesel production and catalyst preparation to propagate the use of renewable energy. In the near future, the world population together with industries would increase drastically and consequently result in a high dependency on oil usage. Hence, many countries are considering the use of WCO as a potential source for biofuel production. For instance, recently the target of the Australian Government is to reduce emissions by about 60 % by 2050 via the utilization of biomass-based resources [108].

Rehan et al. [109] documented that a country like Saudi Arabia holds incredible possibilities to develop waste into biodiesel by making use of several types of bioresources or biomass such as WCO, waste from wood and algae oil and so on, which mostly are diverted to rivers, sea-bodies or landfills. This idea could assist many countries which have great potential in exploiting their biomass resources to shift from a fossil-based economy towards a sustainable bio-based economy.

Biomass-based edible and non-edible oils as stated have been employed as raw materials for biodiesel synthesis, however, edible oil is directly competing with the food supply while non-edible oil requires a large area of land to cultivate if a notable amount of oil is to be recovered. These have also shown that non-edible oil is indirectly competing with food sources, therefore the use of edible and non-edible oil only may not be able to meet the sharp rising in the demand for biodiesel.

The use of high-grade feedstocks results in good-quality biodiesel but remains expensive. Hence, the application of WCO is becoming obvious and indispensable in the pursuit of minimizing the overall cost of production and limiting the competition of biodiesel feedstock with food supply, e.g., in a country like Nigeria with an expected population of 400 million by 2050 [110] in which sources of WCO such as restaurants, homes, hospitals, university restaurants, boarding schools,

Table 7. Advantages and disadvantages of acid, base, and acid-base bifunctional catalysts in waste cooking oil transesterification.

Advantages of heterogeneous catalysts	Disadvantages of heterogeneous catalysts
Acid	*Acid*
– Simultaneous esterification and transesterification of WCO – Not sensitive to water content and FFA in the WCO – It handles both low and high grades of oil – Easy catalyst separation from the end product	– High methanol-to-oil ratio and reaction temperature, hence much energy is required – Tolerance of catalyst during reusability may be low due to the leaching process – Synthesis of the catalyst may be pain taking – Contamination of the product could occur due to leaching and hence, affect the physicochemical properties of the product – The reaction could be slow as compared to the base catalyst
Base	*Base*
– Higher rate of reaction – Tolerance of the catalyst during reusability is high – Corrosiveness is manageable, hence safer – Easy separation from the product after reaction – Mild reaction conditions, hence less energy may be required – Eco-friendly and cheaply obtainable	– Highly sensitive to FFAs present in the WCO – Saponification reaction may occur if not carefully managed, hence, a lower yield of biodiesel will occur – Contamination of products may also occur due to leaching – Poisoning may occur if exposed to air
Bifunctional acid-base	*Bifunctional acid-base*
– It could handle any type of feedstock (both low- and high-grade oil) – If properly designed could be highly stable during reusability – It is not costly if derived from whole biomass – Production of biodiesel with good physicochemical properties is achieved – Not extremely responsive to high water and FFAs – No soap formation	– Synthesis may be complex – Proper composition of the catalyst must be achieved towards a specific purpose – Leaching may occur

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hotels, and roadside food sellers are numerous and large. This makes it easier for feedstock access and the country could probably take advantage of this opportunity to improve the environmental condition. The use of WCO for biodiesel synthesis could be of greater advantage in that it releases less pollutants to the surroundings and supports the principle of cleaner technology.

9 Conclusion

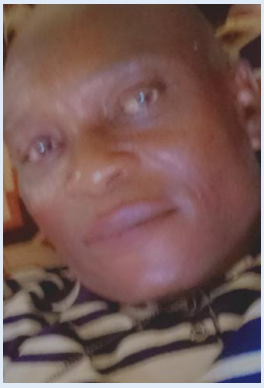
This review highlighted the techniques of producing WCO-biodiesel via diverse types of acid, base, and acid-base heterogeneous bifunctional catalysts. It further discussed the current status and prospects of using biomass-based acid-base bifunctional heterogeneous catalysts for biodiesel production. Existing research in the literature showed bifunctional catalysts to be highly efficient for low-grade feedstocks such as WCO, but with limitations yet to be addressed. Thus, there is a need for reducing the pretreatment cost of WCO as well as developing more efficient bifunctional catalysts that possess the desired properties such as high chemical stability, active sites incapable of leaching away, and promoting catalysts reusability.

Based on this review, it is crucial to consider the following in developing newly improved bifunctional catalysts in the future:

- The development of the bifunctional catalyst should be biomass-derived to mitigate the overall cost of production and enhance environmental sustainability.
- In addition, research that will improve the stability of the acidic-basic active sites on supports should be closely followed to increase the reusability of the catalyst, reduce pretreatment costs, and promote commercialization.

Conflicts of Interest

The authors declare no conflict of interest.



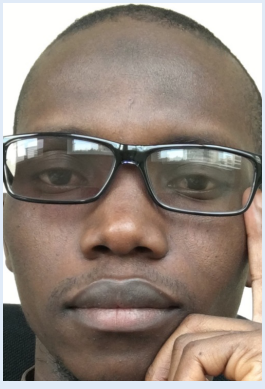
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Acknowledgment

The authors appreciate the Department of Chemical Engineering, University of Ilorin, Nigeria for providing the resources needed.

Abbreviations

AF	animal fat
ASTM	American Standard for Testing and Materials
DMC	dimethyl carbonate
EFB	empty fruit bunch
FAME	fatty acid methyl ester
FFA	free fatty acid
GC	glycerol carbonate
GDC	glycerol dicarbonate
HCV	high calorific value
HLD	hydrophile lipophile balance
JO	jatropha oil
LDL	low-density lipoprotein
MO	microalgae oil
NOx	nitrogen oxide
PO	palm oil
RO	rapeseed oil
SO	soya bean oil
WCO	waste cooking oil
WDF	waste cooking oil-diesel fuel
WP	waste polyolefin

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bi-functional $Fe_2O_3MnOSO_4^{2-}/ZrO_2$nanoparticle solid catalyst, *Fuel* **2015**, *142*, 38–45. DOI: https://doi.org/10.1016/j.fuel.2014.10.038

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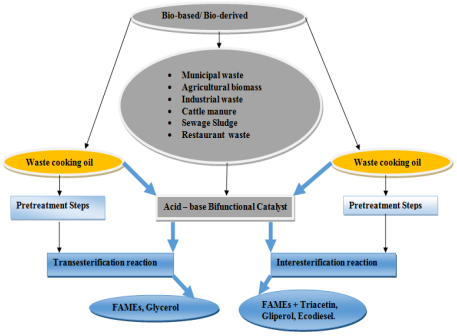
The increase in biodiesel production depends on the availability and sustainability of both feedstocks and catalysts. A biomass feedstock like waste cooking oil which is used together with a biomass-sourced heterogeneous catalyst such as an acid-base bifunctional catalyst, without having to pretreat the waste cooking oil, could give a better quantity and quality of biodiesel in the nearest future.

Waste Cooking Oil Conversion to Biodiesel Using Solid Bifunctional Catalysts

Fatai Alade Aderibigbe, Harvis Bamidele Saka*, Sherif Ishola Mustapha, Mutiu Kolade Amosa, Suleiman Shiru, Idowu Abdulfatai Tijani, Esther Oluwabunmi Babatunde, Bisola Taibat Bello

ChemBioEng Rev. **2023**, *10 (X)*, **XXX** ··· **XXX**

DOI: 10.1002/cben.202200036



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