

Review

# Application of Heterogeneous Catalysts for Biodiesel Production from Microalgal Oil—A Review

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**Abstract:** The depletion of fossil fuel reserves and increased environmental concerns related to fossil fuel production and combustion has forced the global communities to search for renewable fuels. In this regard, microalgae-based biodiesel has been considered as one of the interesting alternatives. Biodiesel production from the cultivation of microalgae is eco-friendly and sustainable. Moreover, microalgae have several advantages over other bioenergy sources, including their good photosynthetic capacity and faster growth rates. The productivity of microalgae per unit land area is also significantly higher than that of terrestrial plants. The produced microalgae biomass is rich with high quality lipids, which can be converted into biodiesel by transesterification reactions. Generally, the transesterification reactions are carried out in the presence of a homogeneous or heterogeneous catalyst. The homogeneous catalysts have many disadvantages, including their single use, slow reaction rate and saponification issues due to the presence of fatty acids in the feedstock. The acidic nature of the homogeneous catalysts also causes equipment corrosion. On the other hand, the heterogeneous catalysts offer several advantages, including their reusability, higher reaction rate and selectivity, easy product/catalyst separation and low cost. Due to these facts, the development of solid phase transesterification catalysts have been receiving growing interest. The present review is focused on the use of heterogeneous catalysts for biodiesel production from microalgal oil as a reliable feedstock with a comparison to other available feedstocks. It also highlights optimal reaction conditions for maximum biodiesel yields, reusability of the solid catalysts, cost, and environmental impact. The superior lipid content of microalgae and the efficient concurrent esterification and transesterification of the solid acid–base catalysts can offer new advancements in biodiesel production.

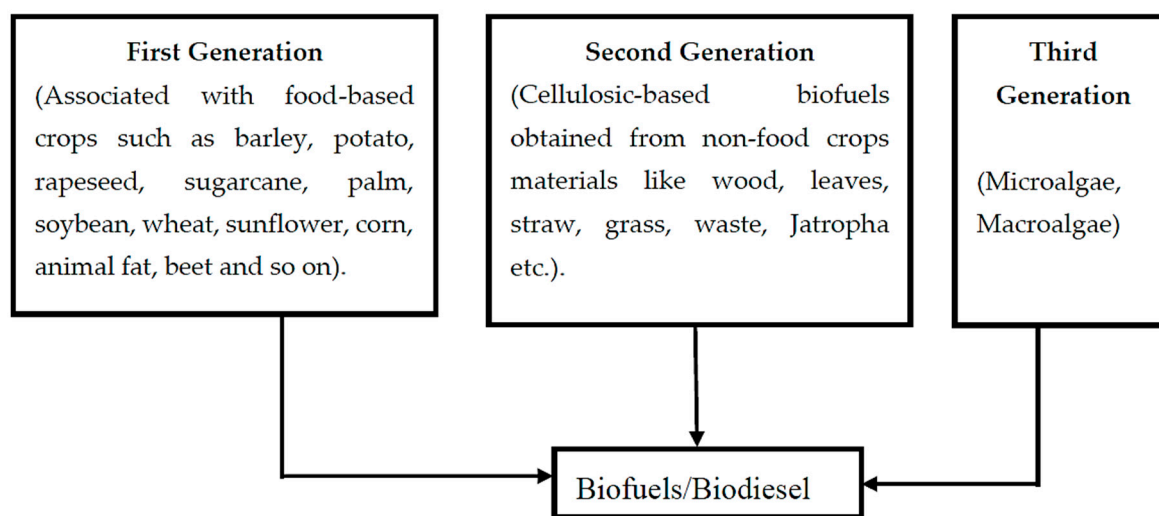
**Keywords:** microalgal oil; transesterification; heterogeneous catalysts; acid–base catalysts; biodiesel

## 1. Introduction

Current worldwide energy resources are mostly based on non-renewable fossil fuels which are the major source of greenhouse gas CO<sub>2</sub> emissions [1,2]. Statistics show that the combustion of fossil fuels contribute approximately 52% to total CO<sub>2</sub> emissions by human activities [3,4]. Therefore, it is necessary to develop alternative energy sources/technologies in order to reduce the greenhouse gas effects drastically [5]. In this regard, renewable energy sources are the potential substitute and the only choice for the ever-increasing challenges [6]. In general, various renewable energy sources such as wind, solar, geothermal, wave, and biofuels are being considered as the alternatives to fossil fuel considering their cleanliness and potential for large scale production [7–10]. Despite having the numerous advantages of renewable energy sources, there are some drawbacks, including availability in specific regions, low efficiency, and high initial and maintenance costs [11,12]. Considering these

different challenges related to renewable energy sources, biodiesel is a promising alternative for petroleum-based diesel fuel [13]. Biodiesel provides a significant return, it is nonhazardous, has an elevated flash point, has a soaring cetane number, high lubricity, little volatility or flammability, superior transport and storage properties, low carbon monoxide production and is eco-friendly [14,15].

Based on origin/feedstocks, biodiesel is categorized as first generation, second generation and third generation (Figure 1). Third generation biodiesels employ macro and micro algal oils as feedstock which are thought to be one of the very hopeful alternative resources for nonedible oils for biodiesel owing to their elevated oil content [16]. Biodiesel is described as methyl (or ethyl) esters of fatty acids produced during a reaction to split the triglyceride in fatty acids [17,18]. This reaction is known as the transesterification or esterification reaction according to the use of basic and acid catalysts [19,20].



**Figure 1.** Generation of Biofuels/Biodiesel.

Conventionally, homogeneous alkaline catalysts,  $\text{CH}_3\text{ONa}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{CH}_3\text{OK}$  are frequently applied for the production of biodiesel [21,22]. Abdullah et al. (2017) reported 93% biodiesel yields from palm oil using  $\text{KOH}$  as a homogeneous catalyst [23]. Chamola et al. (2019) used  $\text{NaOH}$  in transesterification of dry algae and achieved maximum biodiesel yields of 87.42% [24]. Shi et al. (2013) investigated the potentiality of  $\text{CH}_3\text{ONa}$  as a transesterification catalyst of waste chicken fat. Under the studied reaction conditions, the reported conversion of fat was 98.1% [25]. Celante et al. (2018) achieved 99% conversion of soybean oil using  $\text{CH}_3\text{OK}$  catalyst [26]. Saponification and slow reaction rates are the major issues related to the homogeneous catalytic transesterification reactions. In order to secure appreciable reaction rates, the homogeneous catalyzed process requires high quality feedstocks, which must contain the free fatty acid (FFAs) level below 3% by weight. Additionally, the presence of water in feedstock is cumbersome due to the hydrolysis of oils leading to FFAs which ultimately react with alkaline catalysts to produce undesirable soap formation [27]. In addition, during homogeneous catalytic transesterification, the postseparation treatment between the end-product biodiesel and glycerol needs lengthy processes and increases the cost of the end products [28–30].

The heterogeneous catalytic transesterification has several advantages over the homogeneous catalytic transesterification, including easy separation of biodiesel from glycerol, catalyst recycling/reuse, less energy requirement, and minimum consumption of water [21,31]. The solid catalyst to feedstock ratio is also significantly lower than that of the homogeneous catalyst to feedstock ratio. For example, 5.7 tons of solid supported  $\text{MgO}$  catalyst is enough to produce 100,000 tons of biodiesel [32] while 88 tons of  $\text{NaOH}$  is needed as catalyst for the production of 8000 tons of biodiesel [33]. In literature, the alkaline metal oxides such  $\text{CaO}$  [34] and  $\text{MgO}$  [35] are commonly used as solid phase catalyst for transesterification of bio-oils. The use of solid catalysts have been able to overcome a number of challenges of homogeneous catalysts for biodiesel production. Endalew et al. (2011) reported

CaO and Li-CaO as solid phase catalysts for esterification and transesterification of *Jatropha curcas* oil into biodiesel. The catalysts provided complete conversion of *Jatropha curcas* oil under mild reaction conditions, which also helped to maintain the activity of the catalysts for extended periods of time [36]. The transesterification of high fatty acid-containing *Cerbera odollam* was conducted using alumina-supported sulfated zirconia catalysts. The catalyst showed excellent tolerance of high fatty acid concentrations. The biodiesel yield was almost 83.8%, which was significantly higher than that of traditional NaOH catalyst [37]. Viriya-empikul et al. (2012) investigated Ca-based solid catalysts derived from industrial waste for biodiesel production from palm oil [38]. Approximately 94.1% biodiesel yield was achieved when the transesterification was carried out at 60 °C for 2 h.

The present review focuses on the use of solid base, acid, acid–base and biocatalysts for biodiesel production from microalgal oil as the reliable feedstock with comparison to other available feedstock. Furthermore, this review also highlights the suitable heterogeneous catalysts for biodiesel production from microalgae in terms of the yield of biodiesel, optimal reaction conditions, reusability of the catalyst, cost and environmental sustainability [39].

## 2. Microalgae Oil as Feedstock for Biodiesel Production

Microalgae has recently been documented as the most prospective feedstock for biodiesel production [40]. Microalgae are minute photosynthetic organisms that are located in a broad array of ecological settings, on water and land. It has been stated that utilization of microalgae for the production of biodiesel has a high return in terms of lipid content, biodiesel given per acre of farmland for a variety of crops and environmental sustainability [40], although the biodiesel (lipid) contents and its productivity significantly vary among the microalgae species [41].

Among numerous sorts of algae, microalgae appear to be resourceful because: (1) they have lofty increase rates; e.g., repetition in 24 h [42], (2) their lipid content could be customized through shifting the growth medium composition [43], (3) they can be produced more than once a year [44], (4) saline or waste water could be used [44], (5) atmospheric CO<sub>2</sub> is the carbon resource for the growth of microalgae [44], (6) biodiesel produced from algal lipid is nonhazardous and highly eco-friendly [44], (7) microalgae produce 15–300 times extra oil for biodiesel production than customary crops on a regional basis [45]. Predominantly, the microalgae have superior lipid production yields, which have been noticed between 58,000 L/ha to 136,000 L/ha [41].

Moreover, it has a much quicker growth rates than agricultural crops [46,47]. Comparatively, oil from oilseeds such as rapeseed or soybean present oil yields of 974 L/ha and 636 L/ha, respectively. It is noteworthy that the yield of transesterification reaction relies on the character of the lipids. The character of the lipids is vital data for biodiesel making because a number of microalgae can hold up to 93% (g/g lipid) of glycolipids and phospholipids [48]. In addition, microalgae also donate the value to the environment. These organisms can be capable of fastening CO<sub>2</sub> from the atmosphere and thus make a payment to greenhouse gas (GHG) reduction.

Although there is a variety of advantages related with the making of biofuels by means of microalgae, the economic viability of the microalgae-based biofuel industry equivalent to that of either the petroleum or the bioethanol industry has not yet been attained. There is a solitary cause for the elevated production price of algal biofuels. This elevated manufacturing cost of algal biofuels is linked with the different techniques of downstream processing inherent in the production of biodiesel using microalgae [49].

Additionally, while biodiesel is thought to be the major accessible fuel produced from algae, other vital fuel preserves can also be produced, thus making utilization of algae more attractive. Algal oil can be used for producing different types of fuels like bio-gasoline, hydrogen, methane, and ethanol. The biomass-residue is appropriate as a viable feedstock for burning. Additional significant areas of use for algae consist of ecological organization. One variety of algal species possesses an outstanding bioremediation characteristic and consequently, appropriate for nutrient removal from wastewater. Furthermore, algae can be used to produce pigments and fertilizers effectively [50].

### 3. Outline of Biodiesel Production Process from Microalgae

All the current processes for biodiesel production from microalgae comprise a production phase where cells are raised, then separated from the maturing medium followed by lipid removal. Biodiesel or additional biofuels are then produced in a form similar to available processes and knowledge utilized for different biofuel feedstocks [51–53]. Figure 2 illustrates the process flow diagram for biodiesel production from microalgae.

For the processing of biodiesel from a variety of biological resources, transesterification, through a number of successive reversible reactions, is the frequent methodology: triglycerides are transformed stepwise to diglycerides, monoglycerides, and lastly glycerol, with the release of the fatty acid methyl ester distinct as biodiesel at every step in the process. In general, an alcohol and a catalyst are desirable for transesterification of triglycerides [54]. The fundamental reaction of transesterification is illustrated in Figure 3.

The transesterification reaction requires an appropriate catalyst to facilitate the logical conversion rates. The characteristics of the catalysts are important because the reaction situation and post treatment ladder are preset by the characteristic of the catalyst used. Traditionally, the majority of biodiesel is produced with alkaline catalysts, such as NaOH and KOH, owing to their broad accessibility and low price. Although transesterification is practicable with catalysts of a base, the general homogeneous base-catalyzed procedure experiences severe restrictions which transform into increased production expenses intended for biodiesel. Stern feedstock provisions are a major concern with this procedure. The FFA content in the lipid feedstock should not exceed 0.5 wt%, as the higher FFA content causes soap creation, which ultimately hampers fuel grade biodiesel production. FFAs in the feedstock react with metal hydroxide catalyst forming soap (Figure 4a). Gels, which increase viscosity can be raised due to soap formation which greatly increases the product separation cost [55].

Moreover, strict specifications must be followed during the choices of alcohol and catalyst. Total water content of alcohol and catalyst must be within the range of 0.1–0.3 wt% or less for keeping the anhydrous nature [56]. This anhydrous nature is mandatory because it is presumed that feedstock stimulates hydrolysis of the alkyl esters to FFAs in the presence of water (Figure 4b) and, as a result, the creation of soap. The feedstock requirements for base-catalyzed reactions have guided researchers to pursue catalytic and processing substitutes that could ease this complexity and reduce production costs. In this regard, the procedure of acid catalyzed reactions has the capability to overcome this difficulty since acid catalysts do not demonstrate significant vulnerability to FFAs.

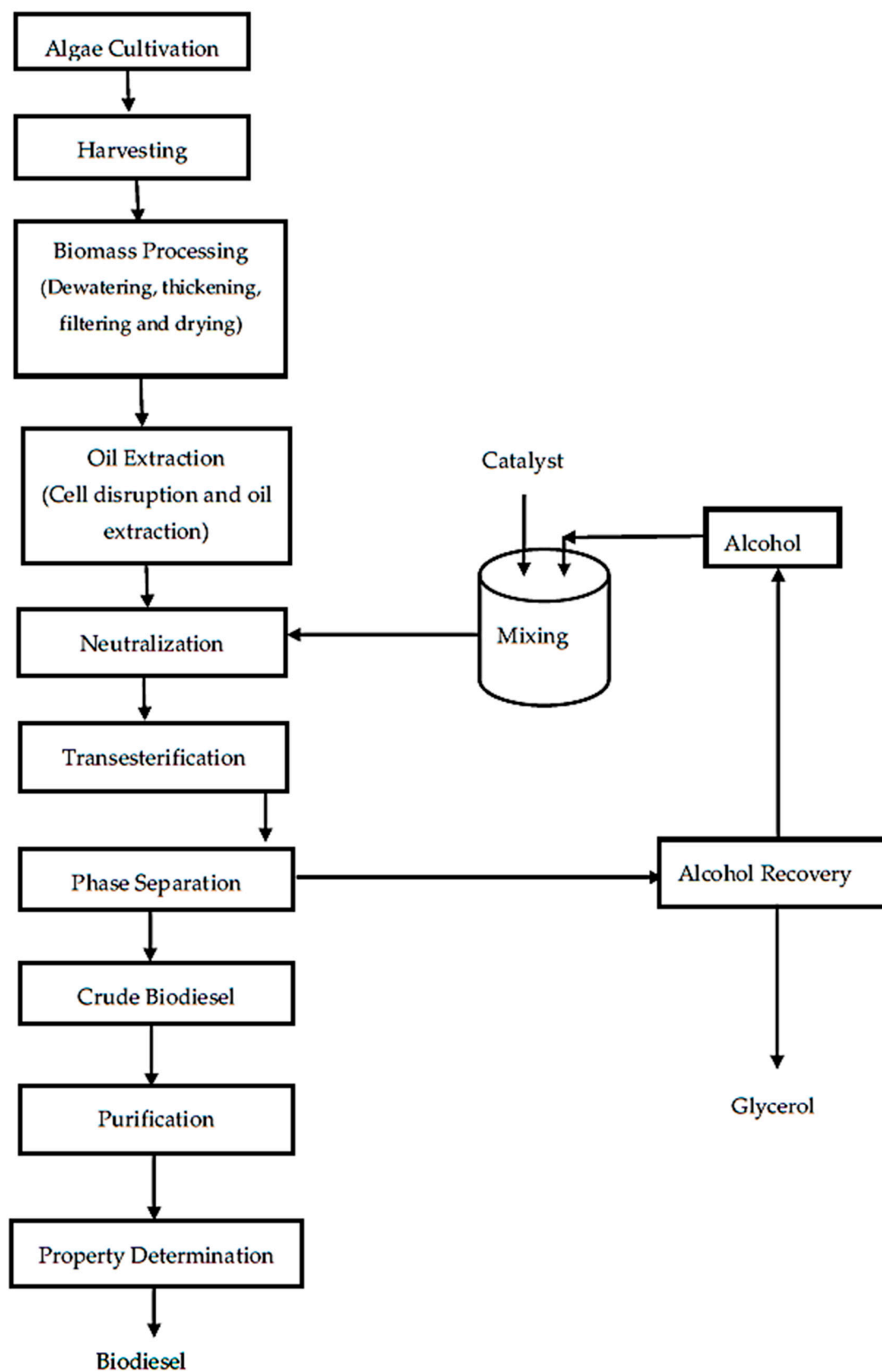


Figure 2. Flowchart of conventional biodiesel production from microalgae.

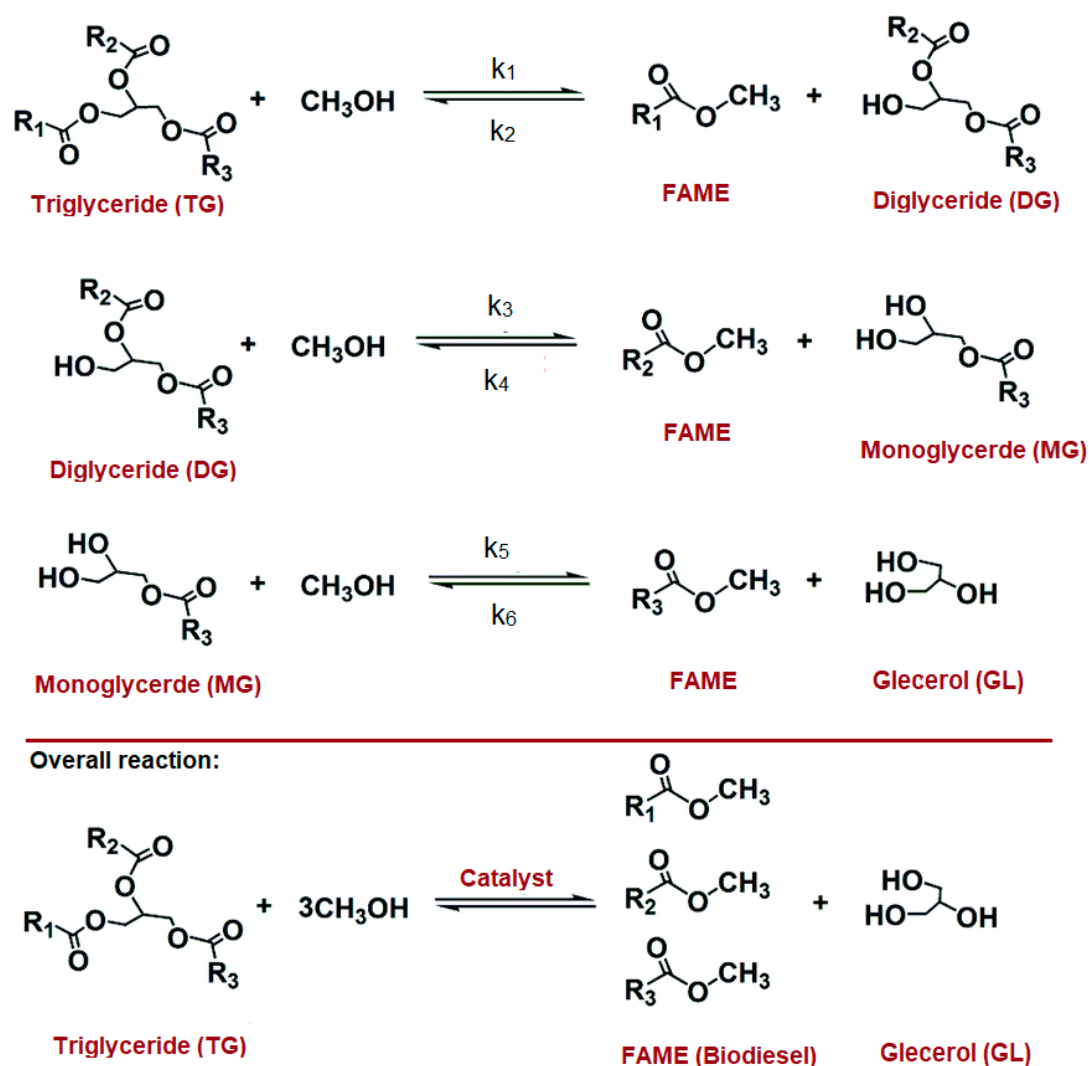


Figure 3. Transesterification reactions of glycerides with methanol.

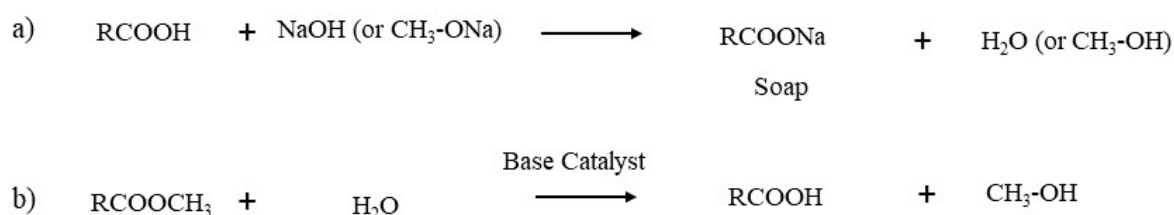


Figure 4. (a) Base catalyst reaction with FFAs to make soap and water, both unwanted byproducts. (b) Water supports the creation of FFAs. These, then, can neutralize the catalyst and generate soap, as in (a).

In addition, Diasakou et al. [57] has also stated that the transesterification reaction usually occurred in three steps where triglyceride (TG) reacted with methanol to produce diglycerides (DG), after that diglycerides (DG) again reacted with methanol to produce monoglycerides (MG) and lastly reacted with methanol to yield methyl ester and glycerol (Figure 3). Moreover, Kusdiana et al. [58] recommended a one-step version for the transesterification reactions (as shown in overall reaction in Figure 3). If we consider alcohol, triglycerides, alkyl ester and glycerol as AL, TG, AE, GL are accordingly, Thus, the overall reaction can be presented as:





The rate of reaction of the above equation can be offered by the following rate expression

$$\text{Rate} = - \frac{d(TG)}{dt} \quad (2)$$

where  $TG$  refers to the substance of non-edible oil utilized in that study. In that supercritical alcohol method, three species were well-defined as unalkyl esterified compounds ( $U_{ae}$ ), alkyl esters and glycerol. Unalkyl esterified compounds ( $U_{ae}$ ) which comprise monoglycerides, diglycerides, triglycerides, and unreacted FFA. Thus, above rate expression can be modified as [58]:

$$\text{Rate} = - \frac{d(U_{ae})}{dt} \quad (3)$$

Commonly, the overall reaction rate is articulated in the Arrhenius form as:

$$-\frac{d(U_{ae})}{dt} = A \exp\left(-\frac{E}{RT}\right)(U_{ae})^n(AL)^m \quad (4)$$

The entire reaction is presumed to proceed as first order reaction.

Although homogeneous catalysts are more effective, they can create severe contamination problems that ultimately demand better separation and product purification conventions, which turn into elevated biodiesel production costs as well as feedstock costs. To be economically feasible and to compete commercially with petroleum-based diesel fuel, the synthesis of biodiesel processing needs as few reaction steps as possible and to reduce the number of separation steps. In this context, the use of a vigorous heterogeneous (solid) catalyst is preferable, along with a cost-effective nonedible oil like micro algal oil could be well suited.

A broad variety of catalysts (homogeneous/heterogeneous) can be utilized to produce biodiesel from various raw materials as shown in Figure 5. It is noteworthy that in comparison to homogeneous catalysis, heterogeneous catalysis has been considered as the top option for biodiesel knowledge in the near future. Heterogeneous catalysts can simply be recycled, recovered, and possess environmentally benign behaviors. Nowadays, heterogeneous catalysts have been employed for biodiesel production from nonedible oil and received global interest owing to their outstanding performance. Currently, it is interesting that some of the heterogeneous catalysts can execute concomitant esterification of free fatty acids and transesterification of the triglycerides available within the nonedible oil effectively.

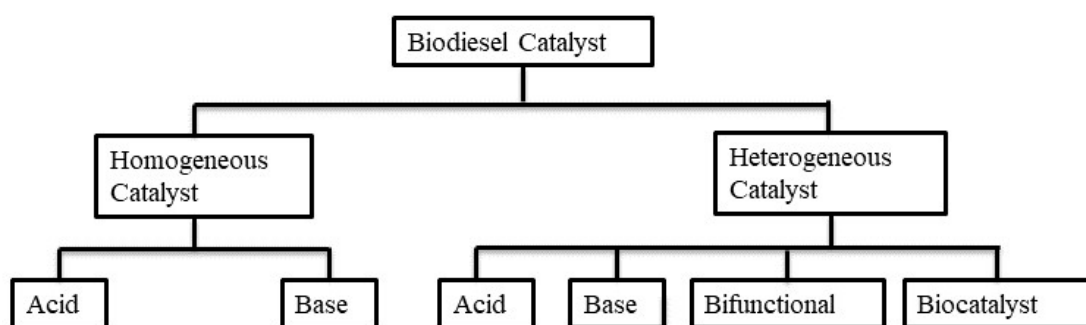


Figure 5. Catalysts used for biodiesel production.

#### 4. Heterogeneous Catalysts for Biodiesel Production

Compared to the homogeneous catalyst, heterogeneous catalysts, which usually appear in solid form, act at a different phase in the reaction mixture of liquid. The homogeneous catalyst is broadly employed in the biofuel industry due to its several advantages, such as high reaction rate, short process time, high accessibility of catalysts [59]. On the contrary, the use of the homogeneous catalyst in esterification and transesterification reactions creates a number of difficulties such as high-cost

post separation processes. To overcome the different problems associated with the utilization of homogeneous bases and liquid acids such as alcoholysis catalysts, many findings were stated to investigate the actions of a variety of heterogeneous materials [50]. Tables 1 and 2 present a list of various solid bases and acid catalysts, respectively, recognized for biodiesel production.

Processing costs can be reduced significantly through the utilization of heterogeneous catalyst because it can be simply recovered, separated and use again [60]. The pivotal features of heterogeneous catalysts are its tuning characteristics that create acidic-basicity, porosity and surface area that can greatly increase the wide range of feedstock for esterification/transesterification process. No additional pretreatment is required for the reduction of the FFA content while using heterogeneous catalysts [61]. Moreover, this can simply catalyze the biodiesel production from high acid oil. Various features of the heterogeneous catalysts (solid acid, solid base, acid–base and biocatalyst) are well studied in this review as each one retains a distinct property to the process.

#### 4.1. Basic Solid Catalysts

Base catalysts are especially appropriate for good purity oils with low FFA contents because they are more vigorous than acids in transesterification. Continuous flow and a packed bed arrangement are generally employed for synthesizing biodiesel using solid base catalyst which ultimately facilitate both coproduction of glycerol with good purity and catalyst separation, thus lessening the production cost and promoting the use of the catalyst again. Supported alkali metals, alkali or alkaline earth oxides, basic zeolites, immobilized organic bases and clays such as hydrotalcites are known as various solid base catalysts [62].

Solid bases, meaning primarily solids with the Brønsted basic and Lewis basic activity centers, that can provide electrons (or accept protons) for (or from) reactants. Synthesis of biodiesel has been carried out intensively over the last ten years through heterogeneous base-catalyzed transesterification using low-qualified oil or fat with FFAs and water. The catalytic efficacy of traditional heterogeneous base catalysts is comparatively minimal and demands to be enhanced. Different sorts of catalytic materials have been tested to enhance the transesterification of glycerides. The commonly studied solid material-based catalysts include hydrotalcites, metal oxides, metallic salt, supported base catalyst and zeolites. As mentioned previously, reactions concerning heterogeneous bases proceed by reactions of either the Lewis or the Brønsted basic sites of the catalyst with a monohydric alcohol (typically ethanol or methanol). The produced alkoxide mixture interacts with triglyceride ester in the oil to yield biodiesel and glycerol in the following steps. Figure 6 shows the mechanism of base-catalyzed transesterification. Solid basic catalysts such as, ZnO, CuO, zeolites, CaO, SrO, MgO, BaO, basic polymers and carbonates such as MgCO<sub>3</sub>, CaCO<sub>3</sub>, BaCO<sub>3</sub> and SrCO<sub>3</sub> have drawn interest as heterogeneous transesterification catalysts.

##### 4.1.1. MgO as a Base Heterogeneous Catalyst

Derivatives of alkaline earth metals and oxides such as Ba, Be, Ca, Mg, Ra, and Sr are applied by various investigators. SrO and MgO are broadly utilized along with the other alkaline earth metals, which have a decent heterogeneous character as a catalyst for biodiesel production [63,64]. Eighteen percent conversion from triacetin feedstock was found for an 8 h reaction time with 600 °C calcination temperature when MgO was utilized as a catalyst by Lopez et al. [65]. This lower amount of conversion is owing to the minimal surface area of the catalyst. In recent times, Di serio et al. [66] used MgO catalyst and noted a 92% biodiesel yield with 5.0 wt% of the catalyst in 1 h, applying a 12:1 methanol to oil molar ratio. Dossin et al. [32] investigated that MgO has the capability to produce five hundred tons of biodiesel in batch reactors through transesterification reaction while maintaining the ambient temperature. Biodiesel manufacture cost is decreased in batch reactors owing to the application of ambient temperatures. Some researchers have revealed that MgO catalyst can give 91% fatty acid methyl ester (FAME) yield in supercritical conditions (300 °C) as well as at a high methanol to oil molar ratio (39.6:1) [66].



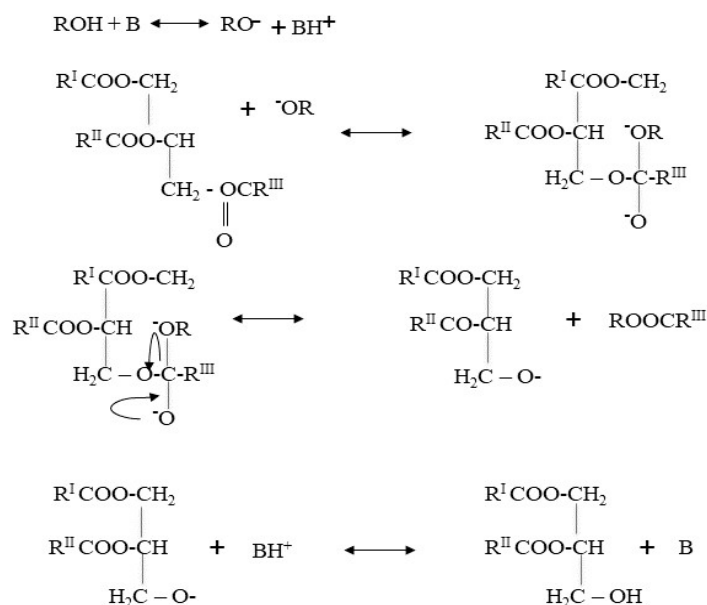


Figure 6. Mechanism of base-catalyzed transesterification.

#### 4.1.2. CaO as a Base Heterogeneous Catalyst

Biodiesel has been produced from soya bean oil by Liu et al. [67] utilizing CaO as the solid base catalyst. He reported some merits of CaO as a solid base catalyst such as lengthening the catalyst's life, high activity and moderate reaction conditions. Nowadays, calcium oxide (CaO) as a heterogeneous catalyst received the attention of the researcher owing to its relatively lower production cost [59,68] and its high basic nature [69]. Liu et al. [67] received ninety five percent conversion of the oil to the ester through transesterification reaction utilizing 8% of CaO with respect to oil mass and a reaction time of three hours, as well as a methanol to oil molar ratio of 12:1. Viola et al. achieved 93% conversion with the same reaction utilizing CaO as the catalyst with 80 min reaction time and 65 °C reaction temperature and applying 5% catalyst with regard to oil and methanol to oil molar ratio of 6:1 [70]. Zhu et al. [71] used a solution of CaO with ammonium carbonate for the conversion of *Jatropha curcas* oil and found 93% conversion. Colombo et al. [34] employed recycling reactors to enhance the production of biodiesel from vegetable oil using CaO as a heterogeneous catalyst. They reported suitable reaction conditions as a 75 min reaction time, a methanol to oil molar ratio of 6:1, and a 3% catalyst mass with respect to oil mass for one hundred percent biodiesel production.

Veljkovic et al. [69] noted the methanolysis of sunflower oil using CaO as a heterogeneous catalyst when applying a 550 °C calcination temperature. They employed 1 wt% catalyst based on oil weight and maintained a two-hour reaction time at 60 °C temperature and found a 98% yield with a 6:1 M ratio of sunflower oil to methanol during transesterification reaction.

Kawashima et al. [72] applied the CaO as heterogeneous catalyst for biodiesel production from rapeseed oil through the transesterification reaction. They treated the CaO in a different way. First, they activated the CaO by a pretreatment with methanol at 25 °C for 1.5 h. In this way, a small amount of CaO could be transferred into Ca(OCH<sub>3</sub>)<sub>2</sub>, which has superior catalytic activity than nonactivated CaO. Later, the Ca(OCH<sub>3</sub>)<sub>2</sub> was utilized to produce FAME and glycerin from rapeseed oil.

Likewise, CaO and modified CaO with Li were studied by Puna et al. [73] to produce biodiesel. They received better catalytic activity as well as stability for both catalysts. In fact, more than 92% biodiesel yields were achieved employing two consecutive batch reactions. Thus, the catalysts are appropriate for the production of biodiesel.

#### 4.1.3. SrO as a Base Heterogeneous Catalyst

Soybean oil was utilized by Liu et al. [74] for transesterification reactions, utilizing SrO metal oxides as a base heterogeneous catalyst. Calcination of SrCO<sub>3</sub> was done at 1200 °C for 5 h for the preparation of the catalyst. Brunauer-Emmett-Teller (BET) surface area and robust basicity were found to be 1.05 m<sup>2</sup>/g and H<sub>+</sub> = 26.5, respectively, from this SrO catalyst. The transesterification reaction was done at 65 °C temperature for 30 min reaction time and obtained 95% biodiesel yield. Moreover, 3 wt% catalyst content and 12:1 molar ratio of methanol to oil was maintained during this reaction. Later, a slight reduction in biodiesel yield was observed for 10 cycles repeated use of SrO catalyst. Figure 7 portrayed the reaction mechanisms as presented by authors. SrO with methanol forms an ionic complex during the major reaction step.

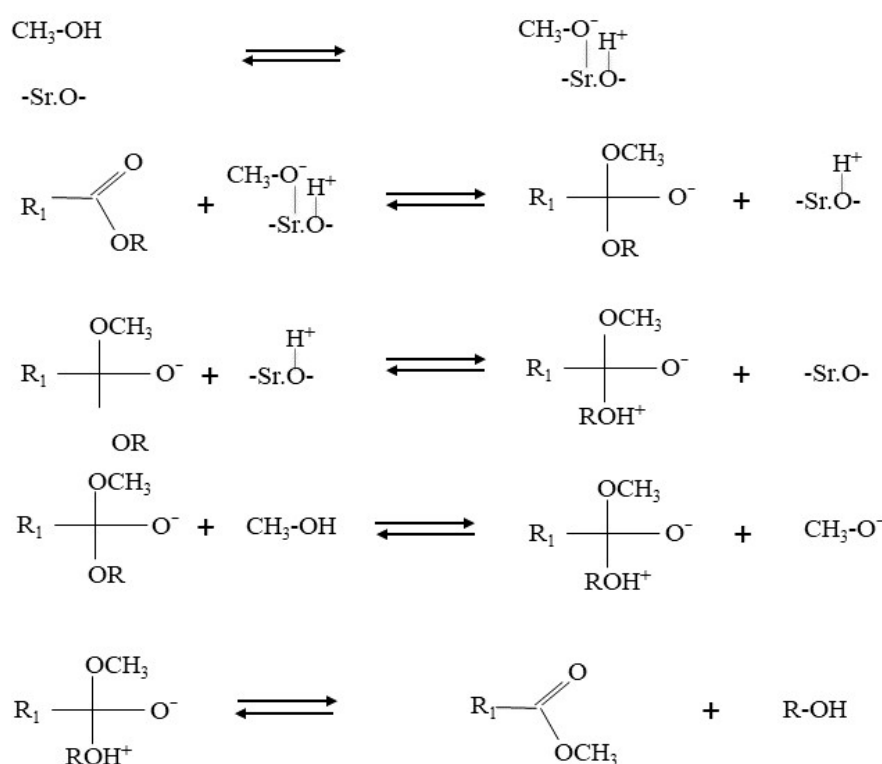


Figure 7. Mechanism of SrO catalyst transesterification.

#### 4.1.4. Biodiesel Production with Mixed Metal Oxide and Derivatives

Two or more metal oxides are generally used to produce a solid mixed-metal-oxide catalyst. The basic concept behind the preparation of solid mixed-metal-oxide catalysts was to increase surface area, augment the basic or acid strength, and improve the stability of these catalysts with respect to single metal oxide.

CaO or MgO are commonly doped with base mixed-metal-oxide to increase their catalytic activity. Catalysts with these types reveal the superior activity during the transesterification reaction in biodiesel production. The presence of a certain amount of free fatty acids (FFA) in the raw material such as oils or fats are thought to be mandatory; if not it can create base catalyst poisoning which ultimately reduces the biodiesel quality [61].

Sol-gel techniques were utilized to prepare the MgO–Al<sub>2</sub>O<sub>3</sub> and CaO–Al<sub>2</sub>O<sub>3</sub> catalysts. These catalysts were found to be efficient during the transesterification of lipids from the microalgae *Nannochloropsis oculata* and achieved 97.5% biodiesel yield at 50 °C reaction temperature and 6:1 methanol–oil ratio [75]. CaO–Al<sub>2</sub>O<sub>3</sub> (80 wt%) was the more active catalyst among these two prepared catalysts and could be recycled at least twice. It was anticipated that the sol-gel synthesis would promote the comparatively high basic strength and site density in the catalysts that would make the

catalysts more reactive and stable. Zabeti et al. (2010) [76] produced a mesoporous CaO/Al<sub>2</sub>O<sub>3</sub> catalyst for biodiesel production from palm oil. They received 98.64% high methyl ester while maintaining an optimized reaction temperature. The optimization was done by applying central composite design (CCD) and response surface methodology (RSM). A large surface area and strong basic sites of the catalyst are considered pivotal factors for high reactivity of catalysts.

Similarly, different investigations were also carried out to alter the characteristics of MgO-based catalysts. For instance, sol-gel technique was applied to produce a sequence of TiO<sub>2</sub>–MgO mixed oxide catalysts and was found to be more efficient for biodiesel production from waste cooking oil, having an acid value of 3.6 mg KOH g<sup>-1</sup>. A 5 wt% TiO<sub>2</sub>–MgO catalyst calcined at 650 °C having a Mg/Ti molar ratio of 1 for 6 h reaction time at 150 °C was employed and achieved more than 85% FAME yield while maintaining a 30:1 methanol to oil molar ratio [77]. The authors stated that the incorporation of a Ti ion reinforced the catalyst stability due to the defects promoted by the replacement of Ti ions for Mg ions. They received consistently better catalytic activity in terms of FAME yield even after four times recycling. Another study applied a coprecipitation method to produce a Mg–Zr solid base catalyst having 2:1 Mg/Zr mass ratio. They calcined the catalyst for four hours at 650 °C. Finally, the obtained catalysts were utilized to produce biodiesel from microalgae *Nannochloropsis oculata* through one-pot transesterification [78].

#### 4.1.5. Biodiesel Production with Transition Metal Oxides and Derivatives

The transesterification rate of solid bases is commonly superior to that of solid acids. Thus, a variety of transition metal oxides with different Lewis properties were tested to produce biodiesel. TiO<sub>2</sub> and MnO are moderate bases revealing better catalytic activity for the production of biodiesel [79]. These catalysts were applied to low grade feedstock having up to 15% high FFA content for the concomitant transesterification of triglycerides and esterification of FFAs while maintaining continuous flow conditions. As a result, in the presence of high FFA, the soap formation associated with metal leaching from the surface of the catalyst was reduced significantly compared to that of traditional base homogeneous catalysts.

#### 4.1.6. Waste Material-Based Heterogeneous Catalysts

Currently, the preparation of heterogeneous catalysts from both biological resources and industrial waste have received attention due to their low cost and good efficiency. These types of natural resources or waste material-derived heterogeneous catalysts showed effectiveness during the transesterification of various oils for biodiesel production. In addition, some authors noted that heterogeneous catalysts obtained from renewable resources revealed their capacity as cost-effective catalysts to produce biodiesel. Table 1 summarizes the commonly investigated basic materials as solid catalysts for transesterification reactions.

Deka et al. [80] obtained a new catalyst from the trunk of *Musa balbisiana* Colla (one variety of banana plant) and utilized it for the conversion of *Thevetia peruviana* seed oil to biodiesel. They achieved 96% conversion of oil to biodiesel using 20 wt% catalyst while maintaining a three-hour reaction time at 32 °C temperature. The catalyst can simply be derived from the waste of harvested banana plants and acts as heterogeneous catalyst. It was noted that after every recycle, catalyst efficiency was reduced successively. Spectroscopic and chemical observation revealed the existence of Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, K<sup>+</sup> and Na<sup>+</sup> as the main components with other relevant metals in ppm level such as Ni, Cr, Mn, Al, Fe, Cu, V, Pd, and Cd. The metals are existing as their oxides, carbonates or chlorides. The surface area of the catalyst was determined using BET technique and found at 1.487 m<sup>2</sup>/g.

**Table 1.** Catalysts utilized as basic solids for transesterification reaction.

Catalyst	Feedstock	Optimum Reaction Conditions			Catalyst Amount	Biodiesel Yield	Reference
		Temp.	Time	Methanol/Oil			
CaO from eggshells	Palm oil	65 °C	2 h	12:1	1.5 wt%	98%	[81]
CaO	Sunflower oil	80 °C	5.5 h	6:1	1 wt%	91%	[82]
KNO <sub>3</sub> /CaO	Rapeseed oil	65 °C	3 h	6:1	1 wt%	98%	[83]
CaO/Al <sub>2</sub> O <sub>3</sub>	Palm oil	64.29 °C	5 h	12.14:1	5.97 wt%	98.64%	[76]
CaO/Fe <sub>3</sub> O <sub>4</sub>	Jatropha curcas oil	70 °C	1.3 h	15:1	2 wt%	95%	[84]
Li/MgO	Soybean oil	60 °C	2 h	12:1	9 wt%	93.9%	[85]
KOH/MgO	Mutton fat	65 °C	0.3 h	22:1	4 wt%	98%	[86]
Dolomite	Palm kernel oil	60 °C	3 h	30:1	6 wt%	98%	[87]
Dolomite	Canola oil	67.5 °C	3 h	6:1	3 wt%	91.78%	[88]
CaMgO and CaZnO	Jatropha curcas oil	65 °C	6 h	15:1	4 wt%	80%	[89]
KF/Ca-Al hydrotalcite	Palm oil	65 °C	5 h	12:1	5 wt%	97.98%	[90]
Mg-Al hydrotalcite	Soybean oil	230 °C	1 h	13:5	5 wt%	90%	[91]
Mg-Al hydrotalcite	Jatropha oil	45 °C	1.5 h	4:1	1 wt%	95.2%	[92]
CaO/mesoporous silica	Soybean oil	60 °C	8 h	16:1	5 wt%	95.2%	[93]
Sodium silicate	Soybean oil	60 °C	1 h	7.5:1	3 wt%	≈100%	[94]

Boro et al. [95] used the waste shells of *Turbonilla striatula* to obtain a solid oxide catalyst and applied it as a renewable heterogeneous catalyst for the conversion of mustard oil to biodiesel. The calcination temperature ranged from 600 to 900 °C for four hours during the preparation of catalyst from the shells and solid CaO formed at 800 °C. It is noted that 93.3% biodiesel yield was achieved from the transesterification of mustard oil using 3 wt% catalyst maintaining 9:1 methanol to oil ratio for a six-hour reaction time at 65 ± 5 °C temperature. The catalyst obtained from the waste shells of *Turbonilla striatula* can be used repeatedly considering gradual loss of catalytic activity during the transesterification of mustard oil.

Wei et al. [96] used waste eggshells for deriving a cost-effective solid catalyst. They calcined the catalyst at 1000 °C and utilized it to produce biodiesel from soybean oil and found good catalytic performance. The transesterification of soybean oil was carried out with 9:1 methanol to oil molar ratio using 3 wt% catalyst and maintaining the reaction temperature at 65 °C for three hours. More than 95% biodiesel was achieved during this transesterification reaction. The catalyst obtained from the eggshell was applied repeatedly during the transesterification reaction and showed no significant loss of catalytic activity until 13 cycles.

#### 4.2. Acidic Solid Catalysts

Acid catalysts express a greater tolerance to FFAs and water than basic homogeneous catalysts such as NaOH and KOH. They have the potential to catalyze both esterification and transesterification concomitantly. It is evident that the reaction with homogeneous acid catalysts are relatively four thousand times slower than that of homogeneous base catalysts [97]. On the other hand, heterogeneous acid catalysts are suitable for low grade feedstocks having high FFAs but showing less catalytic activity. Solid acids can convert low grade fats or oils to biodiesel while maintaining the stable performance of catalysts.

Besides, solid acid catalysts are reactive catalysts for the esterification of FFA to maintain moderate condition before the transesterification reaction. Hence, a pretreatment step using homogeneous

acid catalysts can be avoided. Solid acid catalysts are environmentally friendly and attain the necessary specifications of American Society for Testing Materials (ASTM) standards in produced biodiesel [98]. The solid acid catalyst needs extended time to attain highest conversion rate due to its lower catalytic activity [99].

Few works were stated on heterogeneous acid catalysts as compared to heterogeneous base catalysts. As presented in Table 2, there are different types of solid acid catalysts used in transesterification and esterification reactions comprising sulphonated saccharides, tungsten oxides, sulphonated zirconia (SZ), and Nafionl resins [100]. Muthu et al. [101] utilized sulphated zirconia as a solid acid heterogeneous catalyst for biodiesel production from Neem oil and found 95% biodiesel yield maintaining 9:1 methanol to oil ratio. Shu et al. [102] achieved 94.8% biodiesel yield from waste vegetable oil utilizing carbon-depending solid acid catalyst. Brucato et al. [103] found a 65% biodiesel yield from rapeseed with 40:1 methanol to oil ratio applying a heterogeneous acid catalyst-like titanium-doped amorphous zirconia.

Due to the presence of acid sites with different strengths of Bronsted or Lewis acidity in heterogeneous acid catalysts, industrially it has been considered more effective as contrast to homogeneous acid catalysts. Nafion-NR50, tungstated zirconia and sulphated zirconia are known as solid acid catalysts having enough acid site strength and are particularly preferable as catalysts during the transesterification reaction for biodiesel production [17]. Sulfur containing heterogeneous acid catalysts was investigated by other researchers for transferring acidic oils to biodiesel because sulfur-based acidic homogeneous catalysts like  $H_2SO_4$  revealed a superior acceptance to water and FFA than that of basic homogeneous catalysts (NaOH and KOH), proposing that these catalysts might be best effective for the processing of acidic oils [104].

Zeolites, sulphated zirconia, mixed metal oxides and ion exchange resins were studied by Kiss et al. [105] during esterification reactions. Among them, sulphated zirconia showed higher catalytic activity for esterification reaction. Park et al. [106] applied the sulphated zirconia ( $SO_4^{2-}/ZrO_2$ ) and tungstated zirconia ( $WO_3/ZrO_2$ ) as heterogeneous acid catalysts for effective transfer of the FFA to FAME before the production of biodiesel. Tungstated zirconia ( $WO_3/ZrO_2$ ) is a pellet-type catalyst and was applied for an extended reaction time of 140 h at 75 °C and achieved 65% conversion.

**Table 2.** Acidic solids as catalysts for transesterification reaction.

Catalyst	Feedstock	Optimum Reaction Conditions			Catalyst Amount	Biodiesel Yield	Reference
		Temp	Time	Methanol/Oil			
$SO_4^{2-}/TiO_2-SiO_2$	Acidified cottonseed oil	200 °C	6 h	9:1	3 wt%	92%	[107]
$SO_4^{2-}/ZrO$	Cerberra odollam	180 °C	3 h	8:1	6 wt%	84%	[37]
$SO_4^{2-}/SnO_2-SnO_2$	Jatropha curcas	180 °C	2 h	15:1	3 wt%	97%	[108]
$SO_4^{2-}/SnO_2-SnO_2$	Moringa oleifera	150 °C	2.5 h	5:1	3 wt%	84%	[109]
$SO_4^{2-}/SnO_2-SnO_2$	Croton megalocarpus	180 °C	2 h	15:1	3 wt%	95%	[110]
$ZrO_2-Al_2O_3$	Jatropha curcas	150 °C	4 h	9:1	7.61 wt%	90.32%	[111]
KSF clay Amberlyst	Jatropha curcas	160 °C	6 h	12:1	5 wt%	70%	[112]
Sulfated zirconia (SZ)	Neem oil	65 °C	2 h	9:1	1 wt%	95%	[101]
Carbon-based solid acid catalyst	Waste vegetable oil	220 °C	4.4 h	16.8:1	0.2 wt%	94.8%	[102]

### 4.3. Acid–Base Solid Catalysts

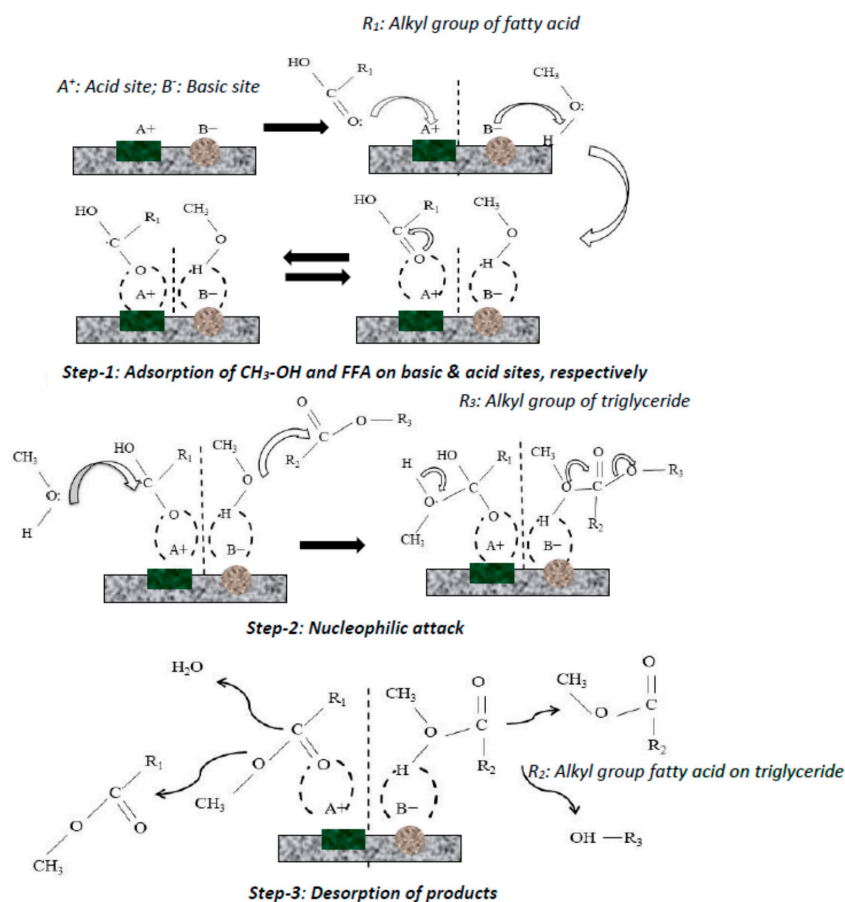
An acid catalyst is required to esterify low grade oil feedstock to reduce the FFA content prior to transesterification during the production of biodiesel. Thus, catalytic science has given more emphasize to synthesizing a novel heterogeneous catalyst having the desired physical and chemical properties to produce biodiesel from a lower quality of oil feedstock. In this regard, a catalyst having an acid–base character, also known as a bifunctional heterogeneous catalyst, has received great attention for different organic reactions in the last ten years. This type of heterogeneous catalyst has the capability to do both concomitant esterification of FFA and transesterification of the triglycerides available in the oil. As this type of catalyst possesses both active acid and base sites on its surface, it cannot be affected by the present water content or produced water content during biodiesel production. Therefore, biodiesel production costs can be reduced efficiently in this way. Besides, this sort of bifunctional heterogeneous catalyst can simply be modified to insert the required catalyst characteristics for reducing adverse effects due to the presence of FFA and water in low grade feedstock during biodiesel production through the transesterification of triglycerides. Figure 8 depicts the common mechanisms of bifunctional heterogeneous catalysts.

Currently, heterogeneous catalysts that have both basic and acidic sites can concomitantly esterify free fatty acids (FFA) and transesterify triglycerides (TG) to biodiesel production [113]. Rabiah et al. [114] stated on a bifunctional heterogeneous catalyst, bismuth (III) oxide ( $\text{Bi}_2\text{O}_3$ ) supported on a lanthanum oxide ( $\text{La}_2\text{O}_3$ ) catalyst, was prepared by a wet impregnation method with 1–7 wt% loading of  $\text{Bi}_2\text{O}_3$ . The  $\text{Bi}_2\text{O}_3$ - $\text{La}_2\text{O}_3$  catalyst exhibited a FAME yield of 93% while maintaining a methanol to oil molar ratio 15:1. In addition, they carried out the reaction for 4 h at 150 °C with 2 wt% catalyst. This catalyst possesses good stability with a strong acid–base nature and achieved 87% conversion after three repeated cycles.

Low grade feedstock like animal fats and waste oils contain FFA and are not suitable for biodiesel production utilizing traditional base facilitated methods due to saponification problems. Bifunctional heterogeneous catalysts possessing both basic and acidic sites were tested to find which could esterify free fatty acids (FFA) and simultaneously transesterify triglycerides (TG) to biodiesel production.

Lin et al. [115] stated the preparation of a mixed metal catalyst of mesoporous calcium silicate with varying amount of calcium oxide. They utilized these catalysts for esterification of free fatty acid (FFA) as well as the transesterification of triglycerides (TG) at the same time. A co-condensation technique was applied during the manufacturing of these catalysts. The mixed metal oxide and tetraethylorthosilicate (TEOS) were reacted in the presence of NaOH where cetyltrimethyl ammonium bromide (CTAB) supplied the micelles template. After separation, the catalyst was calcined for 6 h at 600 °C temperature to make it free from surfactant CTAB. An increased amount of calcium oxide enhanced the structural disorder within the catalyst according to the observation through SEM/TEM. Solid-state NMR revealed that the structure is like crystalline calcium silicate and the total absence of peaks related to CaO was confirmed by XRD analysis. Esterification of soybean oil in methanol was done utilizing this catalyst maintaining a 24 h reaction time at 80 °C temperature and this catalyst can esterify FFA also. The salvaged catalyst can be used again eight times for esterification as well as thirty times for transesterification with no substantial loss of catalytic performance.





**Figure 8.** Common mechanism for concomitant esterification and transesterification reactions on a bifunctional heterogeneous catalyst [116].

Moreover, Lin et al. [117] applied a co-condensation technique for the preparation of mesoporous calcium, barium silicate and magnesium silicate and achieved a patent for their work. They prepared a mixed oxide using weak acidic silica and strong basic metal oxide, and in this way, the acidity of silica was increased significantly. In the calcium silicates mixed oxides, Ca sites were basic, silica sites as Lewis acidic and surface containing hydroxyl group acted as the Brønsted acids. The co-condensation method implemented was analogous to the one stated by others mentioned previously [115]. Three different catalysts, containing varying Ca/Si ratios, effectively transesterify the soybean oil and found 90–100% conversion. Complete conversion occurred at 80 °C temperature, taking 26 h more. All the catalysts showed promising recyclability and no significant loss was found for twenty repeated uses. Bifunctional heterogeneous catalysts for concomitant esterification and transesterification reactions are summarized in Table 3.

**Table 3.** Bifunctional heterogeneous catalysts for concurrent esterification and transesterification reactions.

Catalyst	Feedstock	FFA (wt%)	Optimum Reaction Conditions			Catalyst Amount	Biodiesel Yield	Reference
			Temp °C	Time h	Methanol/Oil			
Bi <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub>	Jatropha curcas	14.5	150	4	15:1	2 wt%	93%	[114]
CaO-La <sub>2</sub> O <sub>3</sub>	Jatropha curcas	14.5	160	3	25:1	3 wt%	98.76%	[118]
K/TiO <sub>2</sub>	Canola oil	-	70	5	36:1	6 wt%	100%	[119]
MgO/TiO <sub>2</sub>	Waste cooking oil	3.6	170	6	50:1	10 wt%	91.6%	[85]
WO <sub>3</sub> /Zr	Sunflower oil	9.1	115.5	2.5	12:1	10 wt%	79.7%	[120]
MCM-41	Waste cooking palm oil	5.08	115.4	1.2	29:1	2.7 wt%	79.7%	[116]
Sr/ZrO <sub>2</sub>	Waste cooking palm oil	5.08	115.4	1.2	29:1	2.7 wt%	79.7%	[116]
MnCeOx	Sunflower oil	0.07	140	5	12:1	1 wt%	≈86%	[121]

## 5. Biocatalysts

Great efforts have been made to examine enzyme catalysts during the transesterification of oils to overcome the saponification problems associated with transesterification of oils having high FFA using a basic catalyst. Enzymatic transesterification can be cost-effective as it acts at a neutral pH with a lower reaction temperature as well as creating only a small amount of soap. Enzymes can be reused as catalysts by being immobilized on solid supports and supplied with a new frame of opportunity. Different techniques usually were applied for enzymatic immobilization such as cross-linking, covalent bonding, and microencapsulation. Lipases are being utilized as a major enzyme during transesterification because they are cost-effective. Lipases have the capability to catalyze both transesterification of triglycerides (TG) and hydrolysis in moderate conditions and are therefore considered for the production of biodiesel [122–124].

It is recognized that lipases can be used for different synthetic reactions comprising transesterification, aminolysis, and esterification. Some special features of lipases such as enantioselectivity, regioselectivity and specificity permit them to catalyze reactions at a moderate pressure and temperature with the formation of little in the way of by-products. Over the last few decades, special care has been taken for the production of biodiesel using lipases as biocatalysts [125,126].

Sarno et al. (2018) utilized the commercially available lipase from *Thermomyces lanuginosus* (TL) immobilized on Fe<sub>3</sub>O<sub>4</sub>/Au in a solvent free system for the production of biodiesel from spent coffee grounds. After three hours the biodiesel yield was 51.7%. The 100% biodiesel yield was achieved within a twenty-four-hour reaction period. The observed reaction kinetics have been considered to be relatively fast. Furthermore, the biocatalyst obtained from the study was applied repeatedly during the transesterification reaction and showed no significant lessening of catalytic activity for three cycles [127]. Saranya et al. (2020) obtained a low-cost biocatalyst by extraction of lipase from *Cladosporium tenuissimum* CS4 fungal strain. After purification, the obtained biocatalyst was applied for biodiesel production from diatomic microalgal oils. Interestingly, the biocatalysts showed superior performance (87%) as compared to the traditional acid catalyst (83%) [128]. Chen et al. (2017) investigated *Pseudomonas mendocina* cells immobilized in a magnetically fluidized bed reactor (MFBR) producing biodiesel from biowaste materials [129]. It showed good reusability in MFBR for ten cycles while maintaining the 87.5% biodiesel yields.

In recent years, nano-biocatalysts have received much attention for the enzymatic production of biodiesel to reduce the massive cost of lipase [130,131]. In this regard, nanomaterials have been broadly utilized for enzyme immobilization [132]. Nanomaterials are predominantly effective means for the advancement of immobilized enzymes due to their large surface area, particle size, and high enzyme loading capacity [133]. Miao et al. (2018) prepared the surface amino-functionalized magnetic nanoparticles (APTES-Fe<sub>3</sub>O<sub>4</sub>) as a immobilization material of lipase and used the glutaraldehyde as a coupling agent for making a covalent bond between lipase APTES-Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles. They obtained 89.4% biodiesel yield during the transesterification reaction under optimum conditions [134]. Nematian et al. (2020) applied the modified nano-biocatalyst for the production of biodiesel from *Chlorella vulgaris* microalgae oil with 35% lipid content. They developed the improved nano-biocatalyst by loading *Rhizopus oryzae* lipase (ROL) on Fe<sub>3</sub>O<sub>4</sub> superparamagnetic nanoparticles (MNPs) with covalent bonding and electrostatic attractions. They reported about 75% fatty acid methyl ester (FAME) conversion using their modified catalyst during the nanocatalyzed transesterification process [135]. Narayanan and Pandey (2018) utilized the nanosilicon immobilized lipase for the production of biodiesel in an improved reverse fluidized bed bioreactor. They mentioned that a more than 80% conversion rate can be achieved in the bioreactor under optimized conditions [136].

## 6. Summary of the Effect of a Heterogeneous Catalyst on the Yield of Biodiesel

Based on review, several investigations were carried out on heterogeneous catalysts with the goal of obtaining solutions to the challenges related to the use of homogeneous catalysts to produce biodiesel. Consequently, a significant number of heterogeneous catalysts have been evaluated and many of them

have shown good catalytic activity. The different heterogeneous catalysts for the transesterification of various feedstocks, along with microalgal oil are summarized in Table 4.

Obviously, microalgae have received great interest as an area of current research for biodiesel production because they have the capability to provide enough fuel for global expenditure [137]. Additionally, due to their high lipid contents and faster growth rate, microalgae could decrease the contest with respect to the use of land for other traditional crops and can reduce the disputes over food-for-fuel. They have the potential to lower the impact of greenhouse gases through CO<sub>2</sub> biofixation. On the other hand, microalgal oil contains high free fatty acids (FFAs) which demand prior treatment if traditional homogeneous catalysts are utilized. A critical survey (Table 4) of the literature proposes that higher biodiesel yields (90–99.5%) can be achieved from microalgal oil applying heterogeneous catalysts. Due to the formation of soap and post-production processes, heterogeneous base catalysts are not well-suited for biodiesel production, thus, the requirement for using solid acid catalysts. However, the solid acid catalyst needs elevated reaction temperatures and prolonged time to attain the highest conversion rate for some cases [99]. In this regard, the bifunctional heterogeneous catalyst with an acid–base character has acquired more attention for different organic reactions at this time [113].

**Table 4.** Various heterogeneous catalysts for transesterification reaction: optimum parameter condition, feedstock, and biodiesel yield.

Feedstock	Catalyst	Optimum Reaction Conditions	Yield (wt%)	Reference
Sunflower oil	Fe–Zn double metal cyanide (DMC)	MeOH/Oil = 15:1, Cat. = 3 wt%, t = 8 h, T = 170 °C	92	[63]
Sunflower oil	ZrO <sub>2</sub> supported La <sub>2</sub> O <sub>3</sub> catalyst	MeOH/Oil = 3:1, Cat. = 2 wt%, t = 5 h, T = 60 °C	84.9	[138]
Soybean oil	ZnO loaded with Sr(NO <sub>3</sub> ) <sub>2</sub>	MeOH/Oil = 12:1, Cat. = 5 wt%, t = 4 h, T = 65 °C	94.7	[139]
Soybean oil	S–ZrO <sub>2</sub>	MeOH/Oil = 20:1, Cat. = 5 wt%, t = 1 h, T = 120 °C	98.6	[140]
Palm oil	CaO from eggshells	MeOH/Oil = 18:1, Cat. = 10 wt%, t = 2 h, T = 65 °C	98	[81]
Palm oil	CaO/Al <sub>2</sub> O <sub>3</sub>	MeOH/Oil = 12:1, Cat. = 1.3 wt%, t = 5 h, T = 64.29 °C	98.64	[76]
Palm oil	KF/Ca–Al hydrotalcite	MeOH/Oil = 12:1, Cat. = 4 wt%, t = 5 h, T = 65 °C	97.98	[90]
Rapeseed oil	KNO <sub>3</sub> /CaO	MeOH/Oil = 6:1, Cat. = 1 wt%, t = 3 h, T = 65 °C	98	[83]
Waste cooking oil	MgO/TiO <sub>2</sub>	MeOH/Oil = 50:1, Cat. = 10 wt%, t = 6 h, T = 170 °C	91.6	[77]
Jatropha oil	Mg–Al hydrotalcite	MeOH/Oil = 4:1, Cat. = 1 wt%, t = 1.5 h, T = 45 °C	95.2	[141]
Soybean oil	Sodium silicate	MeOH/Oil = 7.5:1, Cat. = 3 wt%, t = 1 h, T = 60 °C	100	[94]
<i>Moringa oleifera</i> oil	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -SiO <sub>2</sub>	MeOH/Oil = 19.5:1, Cat. = 3 wt%, t = 2.5 h, T = 150 °C	84	[109]
Purified palm oil	SO <sub>4</sub> -ZrO <sub>2</sub>	MeOH/Oil = 25:1, Cat. = 0.5 wt%, t = 10 min, T = 250 °C	90	[142]
Sunflower oil	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SiO <sub>2</sub>	Ethanol/Oil = 12:1, Cat. = 4.6 wt%, t = 6 h, T = 200 °C	91.5	[120]
Cottonseed oil	Carbon based solid acid	MeOH/Oil = 16.8:1, Cat. = 0.2 wt%, t = 4.5 h, T = 220 °C	94.8	[102]
Croton megalocarpus oil	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -SiO <sub>2</sub>	MeOH/Oil = 15:1, Cat. = 3 wt%, t = 2 h, T = 180 °C	95	[110]
Algae oil	Zirconia, titania	Not reported	90.20	[143]
Algae oil	4% NiO, 18% MoO <sub>3</sub> /alumina	T = 370 °C	99.00	[144]
Algae oil	Amberlyst-15	Not reported	98	[145]
Algae oil	Hierarchical H-Beta zeolites	Not reported	99.5	[144]
Algae oil	Microporous titania	Not reported	94.7	[144]
Microalgal's lipid	Modified Alumina	Not reported	97.5	[75]
Freshwater microalgae oil	Modified titania	Not reported	95	[64]

## 7. Conclusions

Biodiesel is a sustainable, renewable, and environmentally benign alternative fuel for diesel engines. Transesterification of vegetable oil and animal fats or algal oil in the presence of methanol using a suitable catalyst are good practices for the production of biodiesel. Microalgal lipid is mostly triacylglyceride that can be transformed into biodiesel as fatty acid methyl esters via transesterification. Transesterification reactions face some challenges connected to the existence of free fatty acid (FFA) in the feedstock and the biphasic (immiscible) character of the reactants like methanol oil. The advancement of efficient and economical catalysts with an environmentally benign process are essential to overcome the problems associated with biodiesel production from microalgal oil. Recently, despite a few difficulties, heterogeneous catalysts have shown a promising nature over homogeneous catalysts for biodiesel production from third generation feedstock like microalgae. More effective catalytic practices need improvement in terms of catalyst activity and selectivity. Enzymatic catalysts, though highly promising, have a rather slow rate of biological reactions. In this context, the occurrence of basic and acidic sites on the surface of heterogeneous acid–base catalysts could be the best option for future developments in order to produce biodiesel from algal oil. Acid–base catalysts are one of the potential catalysts due to their ability to catalyze both free fatty acids (FFAs) in esterification reactions and triglycerides (TG) in transesterification reactions at the same time. For an effective commercial catalyst, recyclability, lower costs, and catalyst lifetime are highly essential as these have a straightforward impact on the total cost of the process related with biodiesel production.

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