Widely used catalysts in biodiesel production: A review

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Abstract

An ever-increasing energy demand and environmental problems associated with exhaustible fossil fuels have led to the search for an alternative renewable source of energy. In this context, biodiesel has attracted attention worldwide as an alternative to fossil fuel for being renewable, non-toxic, biodegradable, carbon-neutral; hence eco-friendly. Despite homogeneous catalyst has its own merits, currently, much attention has been paid to chemically synthesize heterogeneous catalysts for biodiesel production as it can be tuned as per specific requirement, easily recovered, thus enhance reusability. Recently, biomass-derived heterogeneous catalysts have risen to the forefront of biodiesel productions because of their sustainable, economical and eco-friendly nature. Further, nano and bifunctional catalysts have emerged as a powerful catalyst largely due to their high surface area and potential to convert free fatty acids and triglycerides to biodiesel, respectively. This review highlighted the latest synthesis routes of various types of catalysts including acidic, basic, bifunctional and nanocatalysts derived from different chemicals as well as biomass. In addition, the impacts of different methods of preparation of catalysts on the yield of biodiesel are also discussed in details.

Highlights

- Biodiesel has attracted immense attention as a potential substitute for fossil fuels.

- Esterification and transesterification reactions to produce biodiesel are discussed.

- Effects of various reaction parameters in biodiesel production processes are highlighted.

- Review on the different characterization techniques employed in biodiesel production processes.

- Acid, basic and bifunctional catalysts employed in biodiesel productions are highlighted.

- Different sources, methods of preparation and activities of catalysts are reviewed.

Keywords: Biodiesel, Homogeneous catalyst, Heterogeneous catalyst, Characterization, Fatty acid methyl esters, Renewable energy

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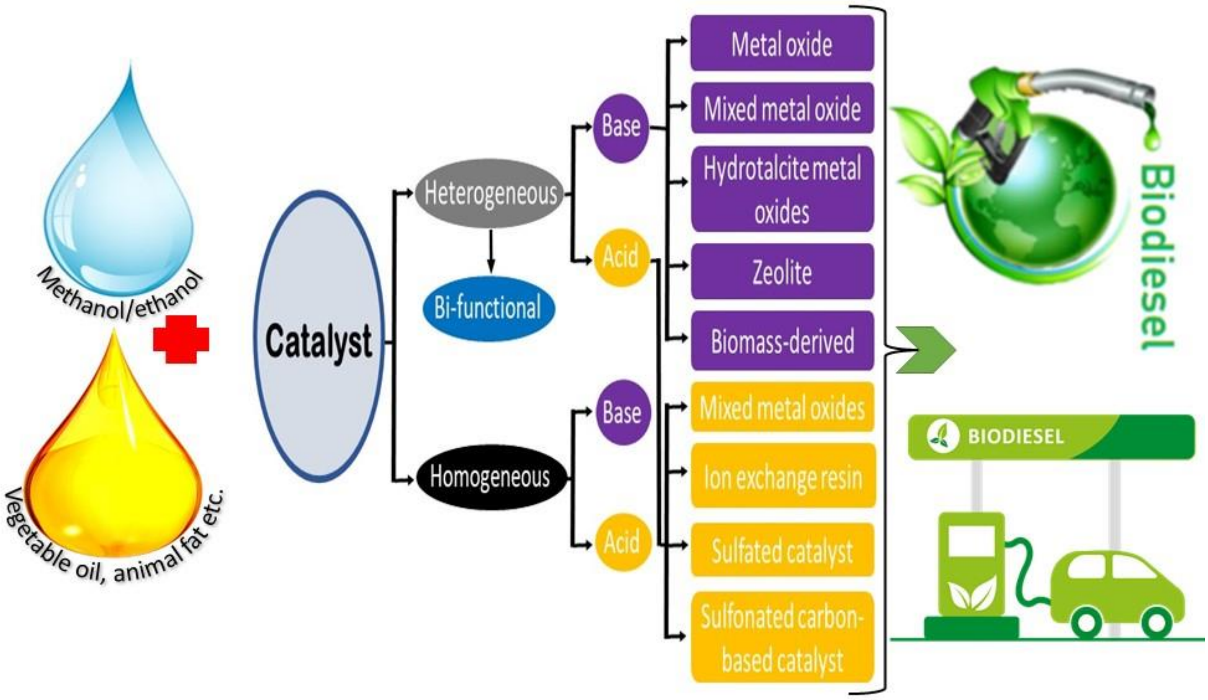


1. Introduction

The exponential growth of the world's population coupled with the high standard of living has resulted in a steep increase in energy consumption [1],[2]. The world's total primary energy consumed (TPEC), which is over 150,000,000 GW h in the year 2015, is estimated to rise by a triggering 57 % in 2050 [3]. Currently, the transportation of goods and services, which is the major contributor to the global economy, primarily rely on non-renewable fossil fuels. In total primary energy consumption, 80 % of the energy consumed is associated with petroleum resources. Amongst these, 54 % is consumed in the transportation sector [4]. It has been predicted that energy consumption in the transportation section will increase with an average rate of 1.1 % per year. As a result, the high energy consumption of non-renewable petroleum-based fuel to fulfil increasing energy demand of human society has led to an ecological imbalance, excess greenhouse gas emission, acid rain, global warming and drastic decline in fossil fuel reserves. These negative factors associated with excessive consumption and exhaustible nature of fossil fuels compel scientific communities to look out for an alternative energy source [5],[6].

Biofuels are an excellent source of energy and widely seen as a potential substitute for fossil fuels. They are prepared from renewable sources such as plants, municipal wastes, agricultural crops, agricultural and forestry by-product [7]. Over the last few decades, biofuel such as biodiesel has gained significant attention as an alternative fuel in the research field because of its sustainable and environment-friendly nature. Biodiesel has exhibited properties similar to conventional fossil fuels (petro-diesel) and has some properties better than petro-diesel such as high combustion efficiency, high flash point, high cetane number, lower CO_2 emission, lower sulfur content and better lubrication [8,9]. The high flash point of biodiesel (423 K), as compared to petrodiesel (337 K), makes it non-flammable and non-explosive resulting in easy and safe handling, storage, and transportation. Additionally, it can be directly used in the automotive engine without any additional alteration [10]. It is estimated that biodiesel demand will increase to double or triple by the year 2020 [11]. In the light of this, in the last decades, much attention has been paid to research on biodiesel production with an intension make it more sustainable and economical. An increasing interest in biodiesel is validated by the number of research paper publications in this area as shown in Figure 1. Statistical data analysis in Figure 1 depicted the increasing trend of published research papers in the field of biodiesel. These data were collected in February 2020 from “SciFinder Database” using the keyword “biodiesel”. From a meagre 157 publications in the year 1993, it has exponentially increased to 3725 publications during its peak in 2014.

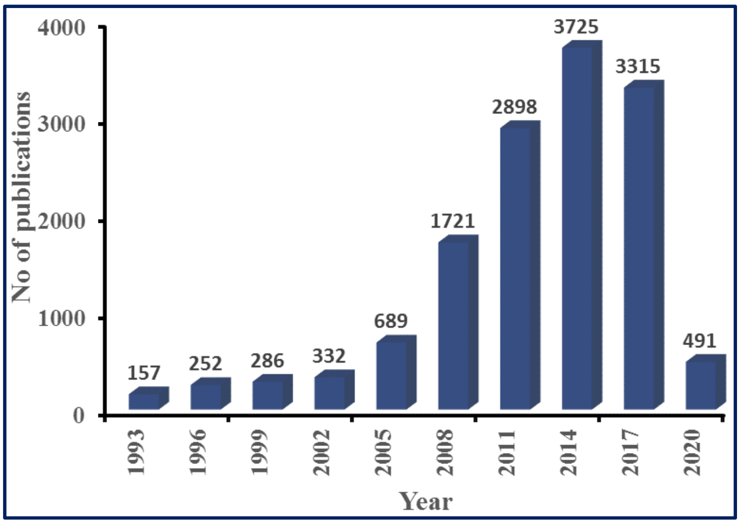


Figure 1: Publications per year for biodiesel during the period 1993 to Feb 2020 (Data collected from SciFinder Database)

2. (Trans)esterification

Transesterification or alcoholysis is a process to produce biodiesel in which edible/non-edible oils or triglyceride (TG) and alcohol have undergone nucleophilic reaction to form fatty acid methyl ester (FAME) and glycerol as a byproduct [12]. The transesterification reaction is illustrated in Scheme 1. Three sequential reversible reactions occurred in the transesterification process; i) conversion of triglyceride to diglyceride, ii) diglyceride conversion to monoglyceride, and finally, iii) monoglyceride conversion to glycerol. An ester is formed in each conversion steps, thus one TG molecule produced three molecules of ester. Transesterification reaction can efficiently convert triglyceride of vegetable oil into FAME, also called biodiesel, as depicted in Scheme 1. However, esterification reaction, a reaction between carboxylic acids and alcohols to afford esters [13],[14],[15], is essential to converts all free fatty acids (FFA) of vegetable oil into biodiesel as shown in Scheme 2. These transesterification and esterification reactions are usually carried out in the two-pots procedure. Usually, the high FFA content of vegetable oil is first converted to esters (FAME) via esterification reaction by employing acid catalyst followed by transesterification reaction using a basic catalyst to converts triglycerides to FAME. However, (trans)esterification reactions (or simultaneous transesterification and esterification) in one-pot is highly desirable to convert both triglycerides and FFA of vegetable oil (with high FFAs) to FAME to reduce time and cost of biodiesel production. The different routes to synthesized biodiesel are outlined in Figure 2.

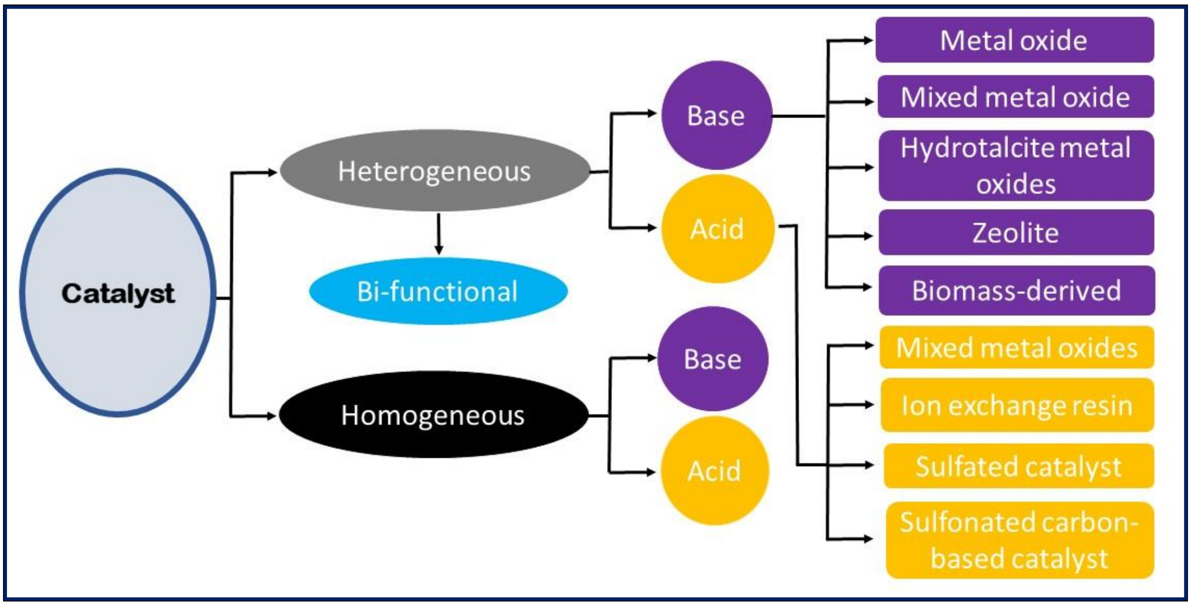
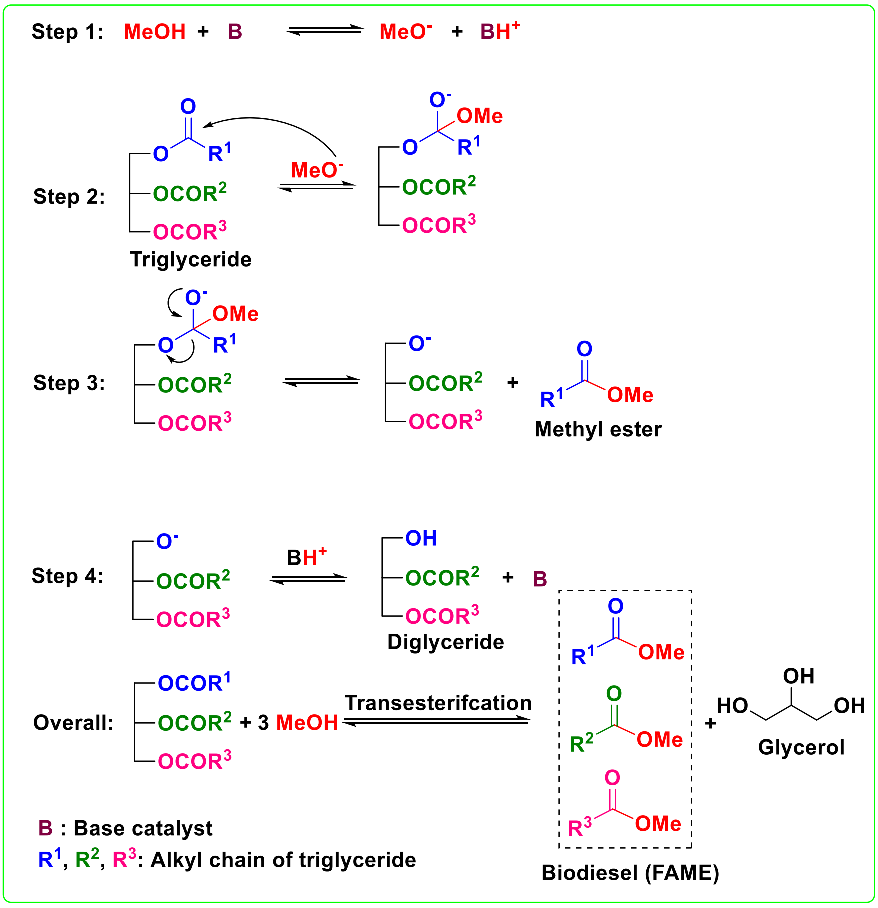


Figure. 2: Catalyst classification for biodiesel synthesis



Scheme 1: Base-catalyzed reaction mechanism for transesterification of TGs of vegetable oil to biodiesel.

Scheme 2: Acid-catalyzed esterification of FFA content of vegetable oil to biodiesel

3. Biodiesel

American Society for Testing and Materials (ASTM) described biodiesel as a mono-alkyl ester produced from edible/non-edible oils or animal fats [16]. Vegetable oils or animal fats comprise of mainly triacylglycerol (TAG) which is an ester of fatty acids (FA) and glycerol. The physicochemical properties of vegetable oils and animal fats are greatly influenced by the compositions of the TAG which further often dictates the quality of biodiesel produced from these resources. FA are classified broadly into two groups: i) saturated FA which has carbon-carbon single bond, and ii) unsaturated FA which comprises of at least one carbon-carbon double bond. The FA most widely found in vegetable oils are oleic acid (18:1), palmitic acid (16:0), linoleic acid (18:2), and linolenic acid (18:3), stearic acid (18:0), palmitoleic acid (16:1), myristic acid (14:0), arachidic acid (20:0). Besides these FA, a trace amount of phospholipids, tocopherols, carotenes, sulphur compounds, and water are also found in vegetable oils [17],[18].

4. Feedstocks for biodiesel production

The feedstocks for production of biodiesel are mainly edible [18],[19],[20] and non-edible vegetable oils [21],[22],[23], waste cooking oils [24],[25], and animal fats including tallow [26], yellow grease [27], lard [28], chicken fat [29],[30] and by-products from the production of Omega-3 fatty acids from fish oil [31],[32]. Algae are another promising feedstocks for biodiesel which have a high potential to replace edible oil due to their availability in a pond, sewage water or in shallow ocean water without dislodging land used for food production [33],[34],[35]. In worldwide, 31 % biodiesel is produced from palm oil, 27 % from soybean oil and 20 % from rapeseed oil [36]. Different countries used various feedstock based on their local availability. The major feedstocks used in various countries are listed in Table 1. The feedstocks cost alone contributed 75 % of biodiesel cost [37]. Thus, proper selection of feedstocks for biodiesel is necessary to reduce the overall cost of biodiesel production. Ironically, utilization of edible oils (sunflower, rape, soy, etc.) as feedstocks for biodiesel, called the first-generation biofuels, resulted in food versus fuel problem and also disturbed the agricultural farmland allocation [27],[38]. In Malaysia, the edible palm oil price has increased by 70 % due to its uses as feedstock in biodiesel industry [39]. In this regard, to mitigate the problem associated with food versus fuel nexus and high cost of first-generation biodiesel, currently, non-edible oil are largely targeted as a biodiesel feedstock. Another problem associated with first-generation biofuels is their remarkably higher cost than fossil fuels. Hence, to bring the cost of biodiesel, utilization of non-edible oil as biodiesel feedstocks is highly relevant. Non-edible oil of more than 300 species are available in South Asia. India has abundant amount (approximately 1 million tons per year) of such non-edible oils. *Pongamia Pinnata* (Karanja) and *Jatropha curcas* oils (JCO) were identified as the most promising feedstocks by the Government of India. However, in India's biodiesel program, Jatropha has got prominence over Karanja due to its less gestation period. If properly managed, non-edible crops planted in different parts of the world has the potential to reduce our dependence on fossil fuel for energy sources and edible oil as biodiesel feedstocks.

Biodiesel has been widely used biofuels in the European Union (EU) and 49 % of biodiesel were produced from rapeseed oil in 2015 in EU [40]. With the increasing uses of waste cooking oil (WCO), recycled vegetable oils and palm oils, the share of rapeseed oil in biodiesel production decreased from 72 % in 2008. To reduce our dependency on edible oil and reduce the price of biodiesel, EU has raised the share of WCO to 2nd position after rapeseed oil in 2015 [41]. The top five biodiesel producer in EU are Germany, France, Spain, Netherlands, and Poland. Germany is the largest biodiesel producer in EU and its production capacity increased from 3.2 billion litres in 2010 to 3.8 billion litres in 2014 [42].

Table 1: Countrywise feedstocks used for biodiesel production.

Country	**Feedstock**
India	Jatropha/ *Pongamia Pinnata* (Karanja) / Soybean/ Rapeseed/ Sunflower
Argentina	Soybeans
Brazil	Soybeans/ Palm oil/ Castor/ Cotton oil
France	Rapeseed/ Sunflower
Peru	Palm/ Jatropha
Germany	Rapeseed
Spain	Linseed oil/ Sunflower
Italy	Rapeseed/ Sunflower
Turkey	Sunflower/ Rapeseed
Greece	Cottonseed
Sweden	Rapeseed
Norway	Animal fats
China	Jatropha/ Waste cooking oil/ Rapeseed oil
Indonesia	Palm oil/ Jatropha/ Coconut
Japan	Waste cooking oil
Malaysia	Palm oil
Philippines	Coconut/ Jatropha oil
Bangladesh	Rubber seed/ *Pongamia Pinnata* oil

Pakistan	Jatropha oil
Thailand	Palm/ Jatropha/ Coconut oil
Iran	Palm/ Jatropha/ Castor/ Algae oil
Singapore	Palm oil
Ghana	Palm oil
Zimbabwe	Jatropha oil
Kenya	Castor oil
Mali	Jatropha oil
UK	Rapeseed/waste cooking oil
Ireland	Frying oil/ Animal fat
Canada	Rapeseed/ Animal fat/ Soybean oil
Mexico	Animal fat/ Waste Oil
USA	Soybeans/ Waste oil/ Peanut
Cuba	Jatropha curcas/ Moringa/ Neem oil
Australia	Jatropha/ Pongamia/ Waste cooking oil/ Animal tallow
New Zealand	Waste cooking oil/ Tallow

4.1. Types of feedstock

Wide varieties of feedstocks such as edible plant oils, non-edible oils, waste cooking oils, animal fats, and algal oil have been considered for the synthesis of biodiesel, and are discussed below.

4.1.1. Edible plant oils

Soybean oil [43], sunflower oil [44], rapeseed oil [45], and palm oil [46] are widely utilized as a biodiesel feedstock in numerous nations, for example, Argentina, Brazil, Indonesia, Europe, US, Malaysia etc. At present, an estimated 95 % of the worlds' total biodiesel is produced from sunflower oil, rapeseed oil, and palm oil [47]. Various types of edible oils exploited as feedstocks for the production of biodiesel are recorded in Table 2.

Table 2. Different forms of edible oils utilized to produce biodiesel.

No.	Edible oil for biodiesel production	Plant source	The botanical name of the plant source
1	Sunflower oil	Sunflower	*Helianthus annuus*
2	Rapeseed oil	Rape	*Brassica napus*
3	Soybean oil	Soybean	*Glycine max*
4	Palm oil	Mesocarp of oil palm	*Elaeis guineensis*
5	Coconut oil	Coconut	*Cocos nucifera*

4.1.2 Non-edible plant oils

Recently, non-edible plant oils have been increasingly considered as another promising potential feedstock for biodiesel attributable to their high oil content and low cost. In addition, unlike edible oils, it does not pose ‘food versus fuel’ problem as they can be grown in barren and arid regions which are not suitable for agriculture. Further, non-edible oil plants can grow under harsh conditions and hardly need any attention; thus, reducing the cost involved in cultivation and potentially reduced the cost of biodiesel [48,49]. Some of the commonly investigated non-edible plant oils for biodiesel production include *Jatropha curcas, Pongamia glabra* (Karanja), *Madhuca indica* (Mahua), *Azadirachta indica* (neem), *Moringa oleifera* (moringa seed), *Calophyllum inophyllum*, *Salvadora oleoides* (Pilu), *Nicotiana tabacum* (tobacco), cottonseed oil, Eruca Sativa Gars, terebinth, rubber seed oil, desert date, *Acrocomia aculeate* (macaúba), *Crambe abyssinica* (hochst), linseed oil, rubber seed oil, *Sapium sebiferum* (chinese tallow), *Sapindus mukorossi* (soapnut), *Euphorbia tirucalli* (milk bush), *Calophyllum inophyllum* (polangafish oil, Jojoba, leather pre-fleshings, apricot seed, *Pistacia chinensis* Bunge Seed, sal oil, *Moringa oleifera* and croton megalo-carpus. Amongst all these oil plants, *Jatropha curcas*, *Pongamia glabra* (karanja), *Madhuca indica* (Mahua), *Azadirachta indica* (neem) are commercially available and most largely used in biodiesel production [50].

4.1.3 Waste cooking oil

Biodiesel production from WCO can partially substitute fossil fuels as well as can solve the energy crisis and environmental pollution. Moreover, WCO is cheaper than fresh vegetable oils, consequently, lessen the expense incurred for biodiesel synthesis. WCO can be grouped into two classifications based on their FFA content if the FFA content is >15 %, then it is called brown grease, otherwise, it is named ‘yellow grease’. Annually billion tons of WCO is generated throughout the world. In EU, it is estimated that around 0.7-1 MT WCO were collected per year. Among 80,000 tons of WCO, around 65,000 tons were collected from UK only, basically originating from commercial restaurants and food processing industries. Therefore, disposal of WCO is a major concern which otherwise contaminates water and environment at large. Although some portions of WCO oil were used in the production of soap, major parts of WCO were usually dumped into the river and landfills. In the light of this, the production of biodiesel from WCO not only reduced the cost of biodiesel but also resolved the disposal problem of WCO and minimized environmental pollution.

4.1.4 Animal fats

Animal fats are another feedstocks for biodiesel production that have the potential to reduce the cost of biodiesel. This type of feedstock includes lard, tallow and chicken fat. However, due to the presence of a high quantity of saturated fatty acids, it has some shortcomings both in chemical and physical properties such as poor cloud point, poor pour point and so forth. At the same time, its high saturation level has various advantages such as high cetane number, high oxidation stability etc. Moreover, animal fats are more favourable biodiesel feedstocks as compared to vegetable oils due to their low price.

4.1.5 Algal oil

Currently, microalgae are viewed as one of the most promising feedstocks for the industrial-scale synthesis of biodiesel. Biodiesel production from algal oil is highly sustainable as several strains of microalgae can double in size within hours; thereby have the capacity to create a large number of litres of biodiesel per hectare every year [51]. Additionally, as several microalgal strains can be grown on non-arable land in a saline water medium, their mass cultivating doesn't compete with food production.

5. Characterization of catalysts and biodiesel

Several analytical techniques are employed to characterize both catalysts and FAME produced. Each analytical techniques will be discussed in the upcoming sections as and when relevant. As a preliminary study, Fourier transform infrared spectroscopy (FT-IR) is usually employed to detect the presence of various functional groups in the catalyst, while X-ray diffraction (XRD) can be employed to investigate the crystallinity and qualitative detection of elements present in the catalyst. The surface morphology, particle size and the structure of the catalysts can be investigated using Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The chemical compositions are investigated using Energy-dispersive X-ray spectroscopy (EDX). X-ray fluorescence (XRF) is commonly used for quantitative detection of metal oxides and X-ray photoelectron spectroscopy (XPS) analyses are routinely performed for the quantitative measurement of the elements present in the catalyst and also provide the chemical state information of the catalyst. Surface area, pore volume and pore diameter are usually measured by Brunauer-Emmett-Teller (BET) analysis, whereas the thermal stability of the catalysts is analyzed using thermogravimetric analysis (TGA). The acidity, as well as basicity of the catalysts, are usually investigated using NH_3 and CO_2 temperature-programmed desorption (TPD) analyses. In addition, basicity and acidity of the catalyst can be visualized by Hammett indicators tests and acid-base titration methods. Valuable information about the degree of carbonization and/or aromatization of carbonaceous material used as a catalyst can be obtained using solid-state magic-angle spin-nuclear magnetic resonance (MAS NMR). Likewise, the successful conversion of biodiesel feedstocks to FAME is confirmed using different analytical techniques. Usually, NMR analysis is used as a confirmation tool to identify the formation of FAME. Despite not common, FT-IR analysis can also be used to identify the FAME formation. The chemical components of FAME along with their respective percentage are usually identified using gas chromatography-mass spectroscopy (GC-MS) technique. In addition ^{1}H NMR spectra can be used to give concrete information about the purity of FAME and percentage conversion of vegetable oil to FAME using Knothe and Kenar equation (1).

$$\%\ \text{Conversion} = 100\ X\ \frac{2A_{Me}}{3A_{CH_2}} \qquad (1)$$

Here, A_{Me} and A_{CH_2} are the integration values of methoxy protons and methylene protons of FAME respectively.

6. Biodiesel production process

Biodiesel can be produced by (trans)esterification, thermal cracking and pyrolysis [52],[53],[54],[55]. Amongst all these methods, transesterification is generally utilized for the synthesis of biodiesel [56],[57],[58]. Alkali, acid and enzyme are routinely exploited as a catalyst for the transesterification reactions. These catalysts had their own merits and demerits as compiled in Table 3. Till now, homogeneous base catalysts such as NaOH, KOH are normally utilized for biodiesel synthesis in industrial scale. In the meantime, owing to their capacity to catalyze both esterification/transesterification reactions, a homogeneous acid catalyst such as H_2SO_4 and HCl are generally picked for feedstock having high FFA such as non-edible vegetable oil, WCO and animal fats. Recently, the heterogeneous catalyst has attracted interest to a great extent for biodiesel synthesis because of their easy recyclability and reusability for successive reaction cycles.

Table 3: Points of interest and detriments of different catalyst utilized for transesterification/esterification reaction (Adapted from ref. [59]).

Catalyst types	Examples	Advantages	Disadvantages
Homogeneous			
Alkali	NaOH, KOH	● High reactivity ● Faster reaction rate ● Minimum cost ● Encouraging kinetics ● Moderate working conditions	● Inappropriate for high FFA in feedstocks ● Deactivates in presence of moisture and FFA. ● Requirement of high amount of waste water ● Saponication occurs as a side reaction. ● Non-recyclable ● Corrosive in nature
Acid	H_2SO_4, HCl, HF etc.	■ Non-reactive to moisture and FFA content in oil. ■ Catalyzed simultaneous esterification/transesterification reactions. ■ Avoid formation of soap.	■ Slow reaction rate ■ Long reaction time ■ Equipment corrosion ■ Higher reaction temperature and pressure ■ High alcohol/oil requirement ■ Weak catalytic activity ■ Catalyst is difficult to recycle
Heterogeneous			
Alkali	CaO, SrO, MgO, mixed oxide	● Non-corrosive ● Environmentally benign	● Slow reaction rate compared to homogeneous one

	and hydrotalcite	• Recyclable • Fewer disposal problems • Easy separation • Higher selectivity • Longer catalyst life	• Low FFA requirement in the feedstock (< 1 wt. %) • Highly sensitive to water and FFA • Saponification as side reaction • Soap formation • High volume of wastewater • Leaching of active catalyst sites • Diffusion limitations, • Complex and expensive synthesis route • High cost of catalyst synthesis
Acid	ZrO, TiO, ZnO, ion-exchange resin, sulfonic modified mesostructured silica etc.	▪ Insensitive to FFA and water content in the oil ▪ Catalyzed simultaneous esterification and transesterification reactions ▪ Recyclable, eco-friendly ▪ Non-corrosive to reactor and reactor parts	▪ Moderate reaction rate ▪ Long reaction time ▪ Higher reaction temperature and pressure ▪ High alcohol/oil requirement ▪ Weak catalytic activity ▪ Low acidic site ▪ Low micro porosity ▪ Leaching of active catalyst sites ▪ Diffusion limitations ▪ Complex and expensive synthesis route ▪ High cost of catalyst synthesis

7. Homogeneous catalyst:

The homogeneous catalysts utilized for the transesterification reaction are classified into two groups such as i) base catalysts, for example, NaOH and KOH and ii) acid catalysts such as sulphuric, sulphonic, hydrofluoric, and hydrochloric acids.

7.1 Base catalyst:

Homogeneous base catalysts are most widely investigated in the transesterification of vegetable oil to FAME as they are cheap and easily accessible. Till date, several homogenous base catalysts have been utilized for the synthesis of FAME e.g., KOH, NaOH, $NaOCH_3$ etc. as shown in Table 4. The uses of NaOH and KOH as catalyst showed excellent catalytic activities towards biodiesel production such as minimum reaction time, high biodiesel yield and occurred at ambient temperature and pressure. However, this process has some certain limitations like water is formed as a byproduct, which reduces biodiesel yield. Other than KOH and NaOH, sodium methoxide and potassium methoxide gives better biodiesel performance as water is not formed in these processes. An alkaline catalyst is not suitable for transesterification of vegetable oils with high FFA content (>2 wt. %). However, it is fit for refined vegetable oils with low FFA content (ranging from less than 0.5 wt. % to less than 2 wt. %).

Dmytryshyn *et al.* [60] examined the transesterification of various vegetable oil such as canola oil, green seed canola oil from heat-harmed seeds, handled waste fryer oil and natural waste fryer oil with methanol to afford FAME using KOH catalyst, and reported a biodiesel yield of 51-87 % under the optimum reaction conditions. In another study, KOH was exploited to convert crude rubber oil and palm oil mixture to biodiesel in 98 % yield under the optimum reaction conditions of methanol-to-oil (M/O) molar ratio of 8:1, 2 wt. % of catalyst loading, reaction temperature of 55 °C and 5 h reaction time. The vegetable oil was esterified using acid catalyst prior to a base-catalyzed transesterification process, to get low FFA content vegetable oil [61]. Similarly, KOH was utilized as a catalyst for the transformation of soybean oil to FAME in 96 % yield [62]. Biodiesel production was performed according to the diagram presented in Figure 3 which consists of synthesis and purification steps. Roselle oil [34], rapeseed oil [63], frying oil [64],[65], used olive oil [66], palm kernel [67] and duck tallow [68] were also successfully transesterified to FAME using KOH catalyst. Karmee *et al.* [69] reported the transesterification of *Pongamia pinnata* to FAME in 92 % conversion using base catalyst KOH. Interestingly, the utilization of tetrahydrofuran (THF) as a co-solvent increased the conversion to 95 %.

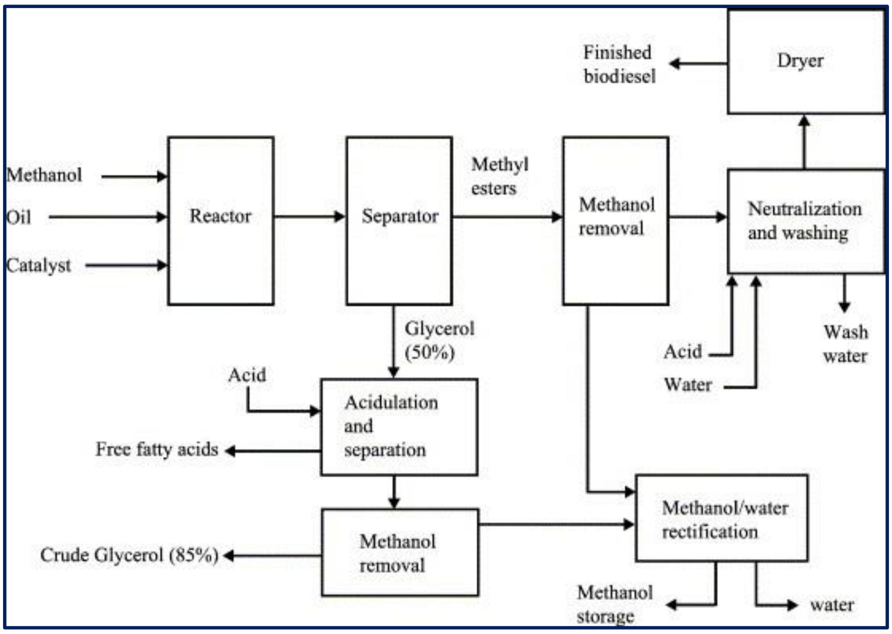


Figure 3: Representative diagram for biodiesel production. Adapted from ref. [58]

Meng *et al.* [24] detailed an exceptionally high activity of NaOH towards biodiesel production from WCO with high FFA in 89.8 % conversion under the reaction settings of 1 wt. % catalyst loading, 6:1 M/O molar ratio, 50 °C reaction temperature and a reaction time of 90 min. The high FFA substance of WCO was reduced by a pre-esterification process with sulphuric acid. Similarly, waste cooking/frying oil [70],[71], canola oil [72], sunflower oil [73], palm oil [74] and cotton seed oil [75] were converted to biodiesel using NaOH as a homogeneous catalyst. Furthermore, $NaOCH_3$ was evaluated as a catalyst for transesterification of rice bran oil to FAME by Rashid *et al.* [72] where 83.3 % biodiesel yield was observed in 60 min under the optimum reaction conditions: 0.88 wt. % catalyst concentration, 7.5:1 M/O molar ratio and 55 °C temperature.

Table 4: Distinctive homogeneous base catalysts utilized for biodiesel production.

No.	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	KOH	Vegetable oil	6:1, 1, 25, 40	51-87	[60]
2.	KOH	Crude rubber/palm oil	8:1, 2, 55, 300	98	[61]
3.	KOH	Soybean oil	6:1, 1, 60, 60	96	[62]
4.	KOH	Roselle oil	8:1, 1.5, 60, 60	99.4	[37]
5.	KOH	Rapeseed	6:1, 1, 65, 120	95-96	[63]
6.	KOH	Frying oil	12:1, 1, 60, 120	72.5	[64]

7.	KOH	Waste Frying oil	6:1, 1, 65, 60	96.15	[65]
8.	KOH	Used olive oil	12:1, 1.26, 25, 90	94	[66]
9.	KOH	Palm kernel	6:1, 1, 60, 60	96	[67]
10.	KOH	Duck tallow	6:1, 1, 65, 180	83.6	[68]
11.	KOH	*Pongamia pinnata*	10:1, 1, 60, 90	92^b	[69]
12.	NaOH	Waste cooking oil	6:1, 1, 50, 90	89.8^b	[24]
13.	NaOH	Waste frying oil	4.8:1, 0.6, 65, 60	98	[70]
14.	NaOH	Waste frying oil	7.5:1, 0.5, 50, 30	96	[71]
15.	NaOH	Canola oil	6:1, 1, 45, 15	98	[72]
16.	NaOH	Sunflower	6:1, 1, 60, 120	97.1	[73]
17.	NaOH	Refined palm oil	6:1, 1, 60, 30	95	[74]
18.	NaOH	Cotton seed oil	6:1, 1, 60, 60	~97	[75]
19.	$NaOCH_3$	Soybean oil	6:1, 0.6, 60, 60	~97	[62]
20.	$NaOCH_3$	Rice bran	7.5:1, 0.88, 55, 60	83.3	[76]
21.	$NaOCH_3$	Waste cooking oil	6:1, 0.75, 65, 90	96.6	[77]

^{a}Methanol-to-oil (M/O) molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

^{b}Conversion

7.2 Acid catalyst:

Base catalysts are usually preferred over acid catalysts as they are more reactive and low cost. However, base catalysts may react with FFA present in the feedstock during transesterification, bringing about soap formation by saponification, which may consume the catalyst and diminish its reactivity. Meanwhile, acidic catalyst is neutral to the FFA and henceforth shows better outcomes for transesterification or esterification of vegetable oils or fats having a high amount of FFA (≥2 wt. %). Generally, acid catalysts are utilized to bring down the FFA content in WCO and animal fats by means of esterification prior to transesterification using base catalyst [5]. H_2SO_4, HCl, H_3PO_4 and sulfonated acids are mostly exploited for the (trans)esterification of vegetable oils [37]. However, acid-catalyzed biodiesel production has some major limitations such as rate of the reaction is almost 4000 times slower than the rate of base-catalyzed transesterification, high alcohol to oil molar ratio required and are very sensitive to the water content as previously reported that a very small amount of 0.1 % is sufficient to affect the esterification reaction [78],[79],[80]. Moreover, it has environmental and corrosive related problems [78]. Because of these demerits, acid-catalyzed biodiesel synthesis is not very popular and is less examined. Some reported literature of acid-catalyzed biodiesel production and their results are listed in Table 5.

Wang *et al.* [79] examined the biodiesel synthesis from WCO and reported a 90 % yield at a higher M/O molar ratio of 20:1, the temperature of 95 °C, 10 h reaction time and 4 wt. % H_2SO_4 catalyst. Moreover, Miao *et al*. [81] examined the conversion of soybean oil to biodiesel using trifluoroacetic acid catalyst and reported 98.4 % biodiesel yield at a reaction time of 300 min, 20:1 M/O molar ratio and 2 molar (2 M) catalyst concentration. Similarly, various edible/non-edible oils such as WCO [82], soybean oil [80], zanthoxylum bungeanum [83] and tobacco seed oil [84] were used for biodiesel production using sulfuric acid. Moreover, trifluoroacetic acid was utilized as a homogeneous acid catalyst for the esterification/transesterification of soybean oil to biodiesel [81]. The catalyst brought about a high biodiesel yield of 98.4 % under the optimum reaction conditions. From the above discussion, it was observed that an acid-catalyzed esterification/transesterification reactions usually require drastic reaction conditions such as high M/O molar ratio, catalyst loading, temperature and long reaction time as compared to base-catalyzed transesterification reactions.

Table 5: Different acidic homogeneous catalysts utilized for biodiesel synthesis.

No.	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	H_2SO_4	Chicken/mutton tallow	30:1, 1.25/2.5, 50/60, 1440	99.01±0.71/ 93.21±5.07	[26]
2.	H_2SO_4	WCO	20:1, 4, 95, 600	90	[79]
3.	H_2SO_4	Used frying oil	3.6:1, 0.1, 65, 40	79.3	[82]
4.	H_2SO_4	Soybean oil	6:1, 3, 60, 2880	98	[80]
5.	H_2SO_4	*Zanthoxylum bungeanum*	24:1, 2, 60, 80	98	[83]
6.	H_2SO_4	Tobacco seed oil	18:1, 1, 60, 25	91	[84]
7.	$C_2HF_3O_2$	Soybean oil	20:1, 2 M, 120, 300	98.4	[81]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

8. Heterogeneous catalysts

Although homogeneous catalyst has its own advantages such as high reactivity and low cost, its utilization in the production of biodiesel is accompanied by several shortfalls such as low quality of glycerol produced, the catalyst cannot be regenerated and the lengthy process involves in the purification of biodiesel; thereby makes the whole process labour-intensive and uneconomical. Hence, in recent years, the heterogeneous catalyst has attracted immense attention for biodiesel production as it can be tailored to match specific requirement, easily recovered and reused for several cycles of catalytic reaction, thereby potentially bring down the labour involved and cost of biodiesel.

Unlike homogeneous catalysts, heterogeneous catalysts mostly appear in a solid form, thus the reaction mixture and the catalyst are in a different phase. In heterogeneous catalyzed reactions, the catalyst surface is the main site for reaction to occurs [85]. The following advantages of utilizing a solid catalyst in transesterification make the process green: i) Catalyst can be reused, ii) very minimal amount of wastewater generated during the process, iii) glycerol separation from the final mixture (glycerol, biodiesel and catalyst) is much easier, iv) high purity glycerol is obtained.

Heterogeneous catalysts have several advantages over a homogeneous catalyst such as simple separation, recyclability and reusability. Moreover, solid catalysts are eco-friendly, less toxic, minimum corrosion and reduced energy intake. Thus, solid catalysts provide an efficient and economical pathway for biodiesel production [12],[86],[87]. Heterogeneous or solid catalysts can be grouped into two categories: i) basic and ii) acidic heterogeneous catalysts. Nowadays, researchers have developed several heterogeneous catalysts, which can promote esterification and transesterification reactions simultaneously in one reaction vessel (one-pot). These type of catalysts are mostly utilized for biodiesel synthesis from the vegetable oils or animal fats having a high amount of FFA without the requirement of additional pretreatment step to reduce the FFA content [12].

8.1 Base catalysts:

In recent years, basic heterogeneous catalysts have been most widely investigated as it can overcome the constraints associated with homogeneous basic catalysts and shows excellent catalytic activity under mild reaction conditions. However, these catalysts are suitable only for biodiesel feedstock with low FFA content, otherwise, catalysts will react with the FFA to produce soap by means of saponification reaction, which make separation of biodiesel from glycerol tedious, thereby diminished biodiesel yield. Several solid base catalysts reported in the literature such as alkaline metal oxide, transition metal oxides, mixed metal oxides, hydrotalcites, zeolites, biomass-based catalyst are discussed comprehensively in this section.

8.1.1 Alkaline earth metal oxides:

Oxides of alkaline earth metal are one of the most widely studied catalysts for biodiesel synthesis due to their insolubility in methanol and low toxicities. The basicity of alkaline earth metal oxides follows the order: MgO < CaO < SrO < BaO. MgO is almost inactive towards the transesterification reaction [87],[88]. Among all alkaline earth metal oxides, CaO is most widely investigated in FAME production due to its high basicity, insolubility in alcohol, non-toxic, cheap and easily available [90]. Nevertheless, it is very sensitive to FFA content and forms undesirable byproducts *via* saponification and also lost its activity in the process [91]. Despite its high activity, SrO is less studied in transesterification reactions as it is very sensitive to the atmospheric moisture and reacts with CO_2 and water to form $SrCO_3$ and $Sr(OH)_2$. Table 6 shows the activity of various alkaline metal oxide towards biodiesel production.

Kouzu *et al.* [91] examined the transesterification of soybean oil using CaO catalyst and reported a high biodiesel yield of 95 % under the optimized reaction conditions: 8 wt. % catalyst loading (with respect to feedstock soybean oil), 12:1 methanol-to-oil (M/O) molar ratio, 3 h time and 65 °C temperature. Granados *et al.* [92] found that CaO calcined at 700 °C showed very high activity towards biodiesel production from sunflower oil and attained 94 % biodiesel yield. Furthermore, the transesterification of rapeseed oil was reported by Kawashima *et al.* [93], where CaO was pretreated with methanol to form $Ca(OCH_3)$, which acted as an initiator for the transesterification reaction. A high biodiesel yield of 90 % was observed using the optimized reaction conditions: catalyst loading of 0.7 wt. %, M/O molar ratio of 3.8:1, time of 2.6 h and temperature of 60 °C. In another work, SrO catalyzed transesterification of soybean oil has been reported by Liu *et al.* [94]. The catalyst showed excellent activity with a high yield of 95 % at 70 °C and 30 min time. The catalyst is highly stable and can be reused for 10 successive cycles.

Ultrasonic-assisted biodiesel synthesis from palm oil was reported using diverse metal oxides such as CaO, BaO and SrO [95]. The activity of the catalyst in ultrasonic-assisted biodiesel synthesis was compared with the traditional magnetic stirring process and found that ultrasonic process showed 95.2 % of yield using BaO within 60 min reaction time, which otherwise take 3-4 h in conventional stirring process. Similarly, ultrasonic-assisted transesterification using CaO and SrO resulted in an increase in biodiesel yield from 5.5 % to 77.3 % and 48.2 % to 95.2 % respectively. These findings show the advantages of using ultrasonication in the field of chemical synthesis particularly in the field of biodiesel synthesis. The authors also investigated the influence of ultrasonic amplitude on the biodiesel synthesis from palm oil and observed that 50 % ultrasonic amplitude displayed the best result in terms of biodiesel yield. Catalyst reusability test revealed that the catalytic activity of BaO decreased drastically, especially in the ultrasonic process during the reusability test, which was mainly due to catalyst leaching. The reaction set-up is depicted in Figure 4.

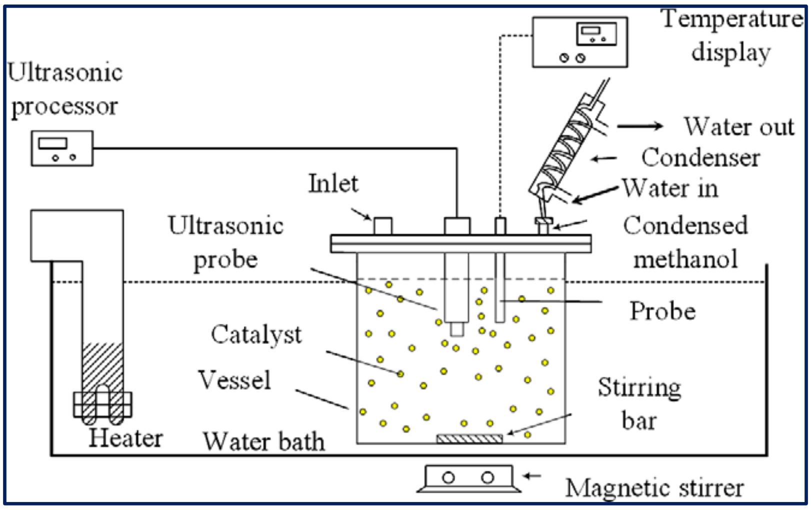


Figure 4: Schematic portrayal of experimental set up for ultrasonic-assisted transesterification reaction. Adapted from ref. [95].

Table 6: Different alkaline earth metal oxide catalyzed biodiesel production under various reaction conditions.

No.	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1	CaO	Soybean oil	12:1, 8, 65, 180	95	[91]
2	CaO	Sunflower oil	13:1, 3, 60, 120	94	[92]
3	CaO	Rapeseed oil	3.8:1, 0.7, 60, 160	90	[93]
4	SrO	Soybean oil	6:1, 3, 70, 30	95	[94]
5	BaO	Palm oil	9:1, 3, 65, 60	95.2	[95]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

8.1.2 Transition metal oxides:

Metal oxides of Zn, Ti, Zr and Zn are most widely investigated in transesterification reactions as they are easily available, highly stable and showed excellent catalytic activities [96],[97],[98]. To date, numerous transition metal oxide-based catalysts have been reported in the field of biodiesel synthesis from vegetable oil as depicted in Table 7. da Silva *et al.* [99] reported Cu(II) and Co(II) impregnated on chitosan catalyst for FAME synthesis from soybean oil. The adsorption process for Cu(II) on chitosan is better than Co(II). However, Co(II)@chitosan showed higher biodiesel yield (94.01 %) as compared to Cu(II)@chitosan (88.82 %) using the reaction conditions of 2 wt. % catalyst loading, 1:5 M/O weight/weight (w/w) ratio and 70 °C temperature. In another work, Jitputti *et al.* [96] investigated ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2 for the FAME synthesis from the crude palm kernel oil and crude coconut oil, and found that SO_4^{2-}/ZrO_2 catalyst displays the highest reactivity for both the oils with biodiesel yield of 90.30 % and 86.30 % respectively. The decreasing order of the catalyst activity towards biodiesel synthesis from crude kernel oil is $SO_4^{2-}/ZrO_2 > SO_4^{2-}/SnO_2 > ZnO > KNO_3/ZrO_2 > KNO_3$/KL zeolite $> ZrO_2$ and for the crude coconut oil is $SO_4^{2-}/ZrO_2 > SO_4^{2-}/SnO_2 > ZnO > KNO_3$/KL zeolite $> KNO_3/ZrO_2 > ZrO_2$.

Meanwhile, Baskar *et al.* [100] used Mn-doped ZnO nanomaterial for the conversion of Mahua oil to biodiesel and observed that catalyst calcined at 600 °C showed highest biodiesel yield of 97 % under the optimum reaction conditions of 8 wt. % catalyst loading, 7:1 M/O molar ratio, 50 min time and 50 °C temperature. The kinetic investigation of the reaction revealed that 181.91 kJ/mol activation energy is necessary for biodiesel synthesis from Mahua oil utilizing Mn-doped ZnO catalyst. The prepared Mn-doped ZnO catalyst was seen as a cluster and spherical in shape as depicted in Figure 5. FI-TR analysis was performed to confirm the formation of biodiesel. Absorption bands at 1744 and 1703 cm^{-1} demonstrated CO stretching of methyl esters in Mahua oil and biodiesel respectively. The main spectrum region that allows for chemical discrimination between Mahua oil and produced biodiesel is in the range 1500-900 cm^{-1} also called known as fingerprint region. Figure 6a revealed the symmetric and asymmetric stretching of alkyl regions at 1376, 1463, 2852, 2922 cm^{-1} and CO group of lactones and esters at 1735 cm^{-1}. Moreover, the stretching band of CO group of typical esters at around 1703 cm^{-1} was observed in Figure 6b. In light of this FT-IR bands, the product obtained after transesterification of Mahua oil using Mn-doped Zno catalyst was confirmed as biodiesel.

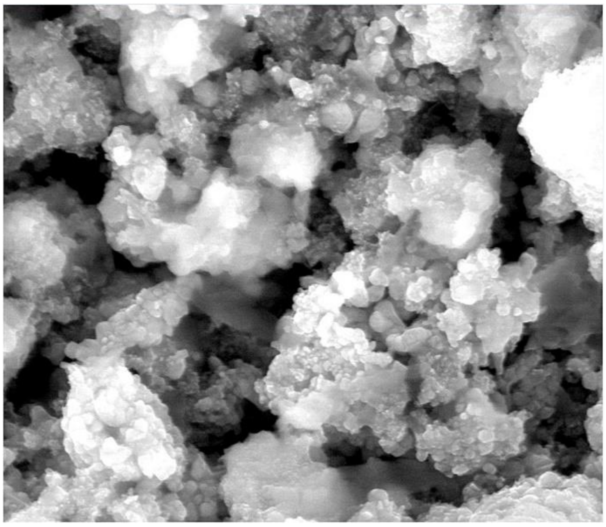


Figure 5: SEM image of Mn-doped ZnO nanocatalyst. Adapted from ref. [100]

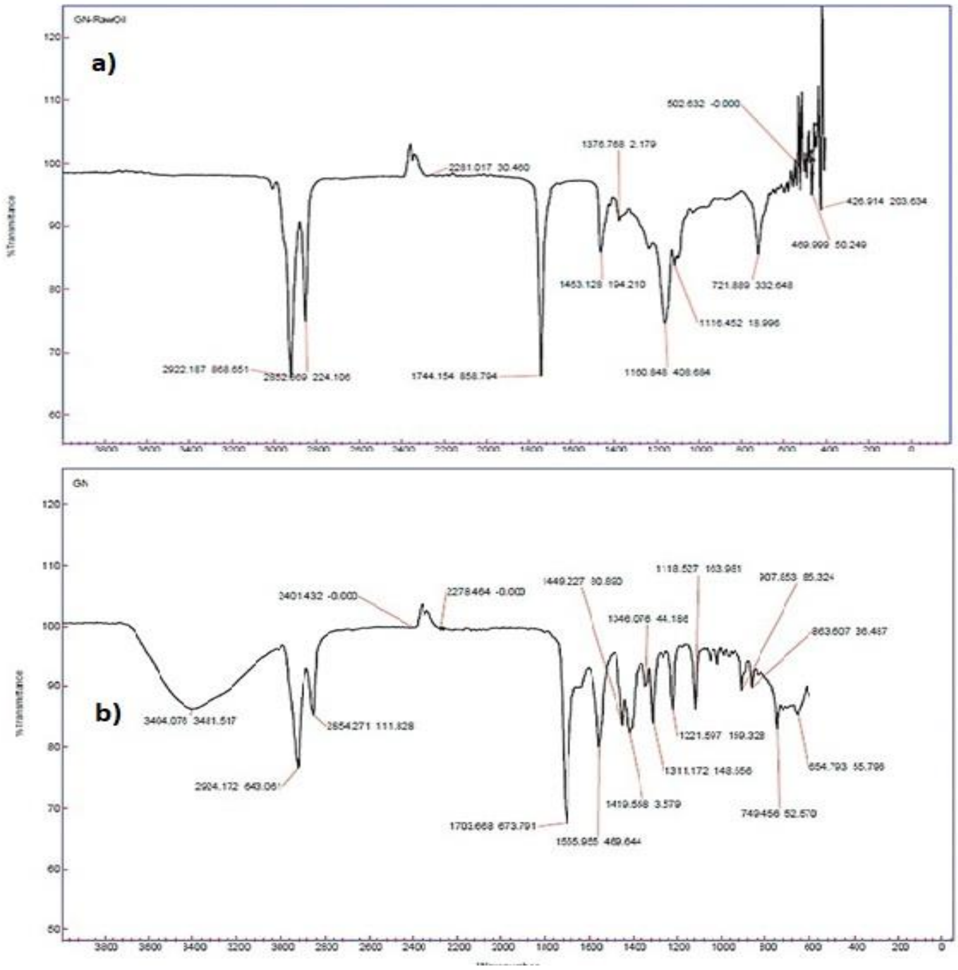


Figure 6: a) FT-IR spectra of fresh Mahua oil. b) biodiesel produced from Mahua oil. Adapted from ref.[100].

Na_2MoO_4 has been synthesized and investigated as a catalyst in transesterification of soybean oil by Nakagaki *et al.* [101] The catalyst displayed high activity towards the transesterification reaction and afforded biodiesel yield of 95.6 %. The high reactivity of the catalyst is due to the acid sites of Mo(VI), which can polarize O-H bond easily. Correspondingly, Serio *et al*. [102] also reported the high reactivity of vanadyl phosphate-based catalyst in the biodiesel synthesis from soybean oil. Regardless of the low surface area, the high reactivity of the catalyst is attributed to the structural/surface morphologies. Biodiesel yield of ≥88 % was recorded using the reaction conditions of 0.5 wt. % catalyst loading, 60 min time and 180 °C temperature. The dehydrated product of the catalyst $VOPO_4.2H_2O$ can be converted to $VOPO_4$ simply by calcination at 400-500 °C.

Table 7: Various transition metal oxide catalyzed biodiesel production under different reaction conditions.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1	Cu(II)@chitosan	Soybean oil	1:5^c, 2, 70, 180	88.82	[99]
2	Co(II)@chitosan	Soybean oil	1:5^c, 2, 70, 180	94.01	[99]
3	SO_4^{2-}/ZrO_2	Crude palm kernel oil	6:1, 3, 200, 60	90.30	[96]
4	SO_4^{2-}/ZrO_2	Crude coconut oil	6:1, 3, 200, 60	86.30	[96]
5	Mn doped ZnO	Mahua oil	7:1, 8, 50, 50	97	[100]
6	Na_2MoO_4	Soybean oil	54:1, 3, 120, 180	95.6	[101]
7	Vanadyl phosphate	Soybean oil	0.88:2, 0.5, 180, 60	≥88	[102]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).
^{c}w/w

8.1.3 Mixed metals oxides:

Mixed metal oxides provide exceptionally fascinating properties especially when each component differs from one another. The basic idea of synthesizing the mixed metal-oxide catalysts is to increase the basic or acid strength, surface area, and stability of these catalysts when compared with single metal oxides. Henceforth, a series of highly efficient, reusable, and stable solid catalysts were prepared. For example, a combination of two metal oxides can show acid-base properties or some unique properties irrespective of their individual properties [103].

To date, several mixed metal oxides have been reported in transesterification reactions and are listed in Table 8.

In 2008, Albuquerque *et al.* synthesized MgO-CaO mixed metal oxides catalyst for the transformation of sunflower oil to biodiesel in 92 % yield under the optimized reaction conditions of M/O ratio12:1, catalyst loading 2.5 wt. %, temperature 60 °C and reaction time of 60 min. In the same year, Kawashima *et al.* [104] investigated various calcium-containing catalysts-$CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaO-CeO_2$ in the biodiesel production from rapeseed oil. Among these, $CaO-CeO_2$ showed excellent results (approximately 90 % yield) with high stability compared to other calcium-containing heterogeneous catalysts under the optimized reaction conditions: 6:1 M/O molar ratio, 10 wt. % catalyst loading, 10 h time and 60 °C temperature. The catalyst can be reused for 7 times with a high yield of >80 % in each time. Sun *et al.* [105] also prepared La_2O_3 loaded ZrO_2 catalyst by varying La_2O_3 amount from 7-28 wt. % and investigated for the synthesis of biodiesel. 21 wt. % La_2O_3 loading on ZrO_2 and calcined at 600 °C demonstrated the highest catalytic activity towards biodiesel production from sunflower oil. The authors proposed a model for the preparation of the catalyst, where $La(NO_3)_3$ was impregnated on the surface of ZrO_2 followed by drying to form a film of $La(NO_3)_3$, which upon calcination forms the La_2O_3/ZrO_2 composite, resulting in a decrease in particle size due to *t/m* phase transition (Figure 7). A high oil conversion of 96 % and 84.9 % FAME yield was observed using 30:1 M/O molar ratio at 200 °C. They reported an excellent activity of catalyst prepared by 21 wt. % loaded La_2O_3 and calcined at 600 °C.

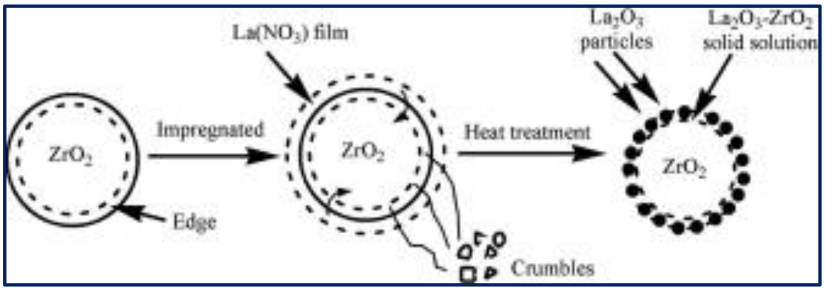
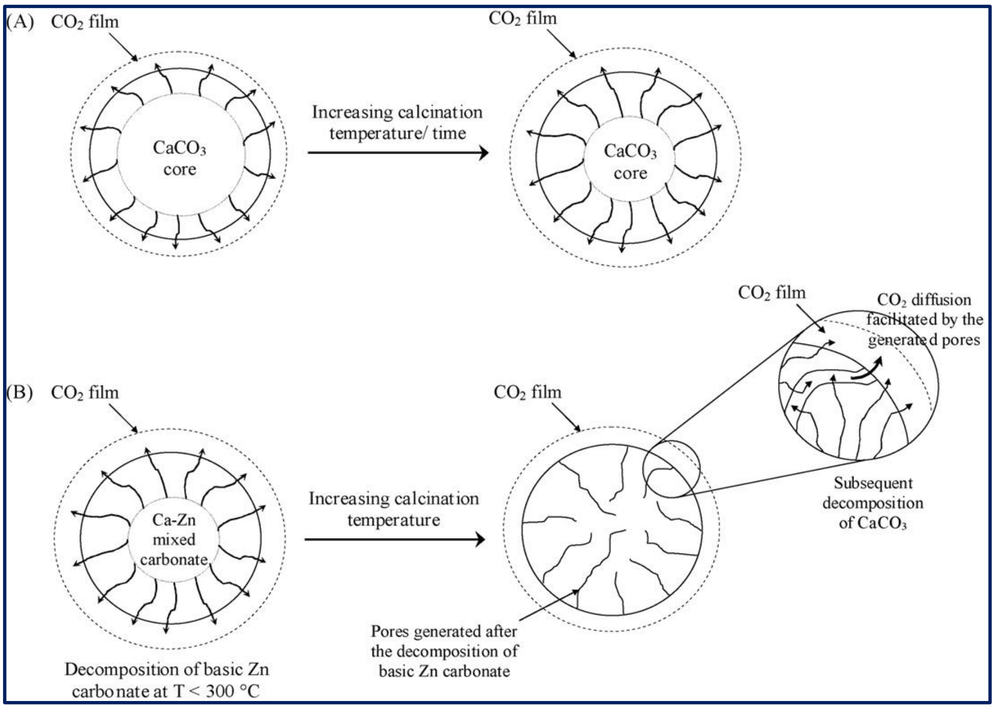


Figure 7: Proposed model for the solid-state reaction on the catalyst surface. Adapted from ref. [105].

Wen *et al.* [106] obtained TiO_2-MgO catalyst *via* the sol-gel method and employed it in the FAME synthesis from WCO. Substitution of Ti to the Mg lattice led to defects in the surface of the catalyst, enhanced both the activity and stability of the catalyst. It was revealed that the catalyst with 1:1 Ti to Mg molar ratio and calcined at 923 K is the most active one in

FAME synthesis. Biodiesel yield of 92.3 % was observed utilizing the catalyst MT-1-923 using the reaction conditions: 10 wt. % catalyst loading, 50:1 M/O molar ratio, 6 h time and 160 °C temperature. Similarly, SrO/SiO_2 and SrO/CaO has been synthesized and their catalytic activity was compared with naked SrO in transesterification of olive oil by Chen *et al.* [107]. Although naked SrO showed very good catalytic activity and afforded 82 % yield in just 15 min, biodiesel yield shrunk to 68.9 % when the reaction was performed for 3 h. They reported that the reason for the unusual decreased in biodiesel yield was due to reverse reaction between FAME and glycerol, which showed that the catalyst not only catalyzed the forward reaction but also catalyzed the reverse reaction as well. On the contrary, modification of SrO with SiO_2 and CaO provided an excellent activity as well as high stability. They observed that around 95 % conversion was obtained at 65 °C using SrO/SiO_2 and SrO/CaO in 10 and 20 min respectively. However, they reported that on decreasing the reaction temperature to 45 °C, SrO/CaO showed only 20.20 % conversion as compared to SrO/SiO_2, which showed 76.9 % conversion. Thus, SrO/SiO_2 displayed better reactivity towards transesterification of olive oil than SrO/CaO and possessed high tolerance to the water content and FFA of biodiesel feedstocks.

In the recent past, Madhuvilakku *et al.* [108] developed TiO_2-ZnO nanocatalyst and utilized in FAME synthesis from palm oil. Arrangement of deformities on the catalyst surface as a result of the substitution of Ti on Zn grid improved the reactivity and stability of the prepared catalyst. They recorded 92 % biodiesel yield was acquired under the optimized reaction conditions. Similarly, a series of ZnO-La_2O_3 catalyst have been examined in the biodiesel synthesis from waste oil by Yan *et al.* [109]. Incorporation of La promoted dispersion of ZnO and improved acidic-basic sites, thereby increased catalytic activity towards both transesterification and esterification reactions. The molar ratio of 3:1 Zn to La showed the highest activity towards biodiesel production. A high 96 % yield was reported under the reaction conditions: 6:1 M/O molar ratio, the reaction temperature of 200 °C and 3 h time. The authors also reported that the catalyst can endure FFA and water contents and thus allowed direct conversion of waste oil to FAME. In another work, transesterification of palm kernel oil to produce biodiesel has also been reported using a mixed metal oxide solid base catalyst CaO-ZnO [110]. Upon incorporation of Zn to the CaO phase, the particle size of the catalyst has decreased and has reduced the calcination temperature required for the decomposition of carbonates to its oxides. Lowering of calcination temperature for the decomposition of $CaCO_3$ upon the incorporation of Zn can be explained by particle size reduction coupled with a loss of H_2O and CO_2 from the zinc carbonate. The schematic representation for the decomposition of $CaCO_3$ and formation of CaO-ZnO mixed metal oxides is displayed in Scheme 3. It is well known that decarbonisation is a reversible process, which mostly depends on atmospheric CO_2, particle size and composition. The dissociation of CO_2 normally occurs in the outer surface (Scheme 3A). Moreover, upon calcination, the evolved CO_2 may form a layer on the surface of the material during the continuous disjunction of inner particles, generated a possibility for recarbonation of CaO to $CaCO_3$ (Scheme 3B). However, incorporation of $ZnCO_3$ resulted in the formation of voids due to its decomposition to zinc oxide. The resulting voids facilitated heat transfer to the interior particles and evaporation of the gaseous compounds. Moreover, due to the small particle size of the CaO-ZnO, the diffusion distance of CO_2 decreased, thus calcination temperature also decreased.



Scheme 3: Proposed models for $CaCO_3$ decomposition to CaO (A) and mixed precipitate of Ca-Zn Adapted from ref. [110].

Among solid base catalysts, solid ZrO_2 catalysts become popular because of their environmentally benign nature and economic viability for biodiesel production. Till date, different types of ZrO_2 catalysts have been developed for use in biodiesel production. In this line, Su *et al.* [111] synthesized microporous solid base MgO-ZrO_2 composites and utilized them as effective heterogeneous catalysts in biodiesel synthesis. They claimed that such microporous catalysts are of great significance as the presence of porous materials in the preparation of these catalysts provided the ability to interact with atoms, ions, molecules.

Recently, Ibrahim *et al.* [112] examined the influence of different support materials like Al_2O_3, Fe_2O_3, TiO_2 and SiO_2 on physicochemical properties and efficacy of ZrO_2 solid catalysts commonly used in biodiesel synthesis. From the results obtained it was revealed that ZrO_2 supported on SiO_2 showed the highest conversion rate due to comparatively high surface area and a high number of Lewis acid sites. In another study, Faria *et al.* [113] developed nanosized catalyst mixed metal oxides SiO_2/ZrO_2 catalyst prepared *via* sol-gel strategy and examined its reactivity in the synthesis of biodiesel from soybean oil. It was observed that this catalyst displayed promising reactivity and gave 96.2 ± 1.4 % biodiesel yield after 3 h of reaction time. In addition, the catalyst can be reused for 6 progressive cycles with little drop in activity.

Table 8: Various mixed metal oxide catalyzed transesterification of vegetable oil.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1.	MgO-CaO	Sunflower oil	12:1, 2.5, 60, 60	92	[57]
2.	$CaO-CeO_2$	Rapeseed oil	6:1, 10, 60, 600	90	[104]
3.	La_2O_3/ZrO_2	Sunflower oil	30:1, 21, 200, 300	84.9	[105]
4.	TiO_2-MgO	WCO	50:1, 10, 160, 360	92.3	[106]
5.	SrO/SiO_2	Olive oil	6:1, 5, 65, 10	95	[107]
6.	SrO/CaO	Olive oil	6:1, 5, 65, 20	95	[107]
7.	TiO_2-ZnO	Palm oil	6:1, 14, 60, 300	92	[108]
8.	$ZnO-La_2O_3$	Waste oil	6:1, 2.3, 200, 180	96	[109]
9.	CaO-ZnO	Palm kernel oil	30:1, 10, 60, 60	>94	[110]
10.	$MgO-ZrO_2$	Soybean oil	20:1, 3, 150, 360	99	[111]
11.	$ZrO_2@SiO_2$	Stearic acid	120:1, 10, 120, 180	48.6	[112]
12.	SiO_2/ZrO_2 NP	Soybean oil	6.6:1, 2.8 mmol, 50, 180	96.2±1.4	[113]

^{a}Methanol-to-oil molar ratio, Catalyst loading (wt. %), Temperature (°C), Reaction time (min).

8.1.4 Hydrotalcite metal oxides:

Recently, hydrotalcites have attracted interest as a solid catalyst in the transesterification reactions due to their tunable properties and excellent performance. They belong to the layered double hydroxide (LDH) family. The general formula of hydrotalcite is $[M_n^{2+} M_m^{3+} (OH)_{2(n+m)}]^{m+} [A^{x-}]_{m/x}.yH_2O$, where M^{2+} is a divalent metal e.g., Ca^{2+}, Zn^{2+}, Mg^{2+} etc., M^{3+} is a trivalent metal, most frequently Al^{3+}, whereas A^{x-} is an anion with x in the range of 0.1-0.5 [114,115]. Table 9 shows various reported hydrotalcite catalysts employed in the biodiesel synthesis from different feedstocks. Navajas *et al.* [116] prepared Mg/Al hydrotalcite with composition within the range of 1.5-5 by co-precipitation method and applied it in the conversion of sunflower oil to biodiesel. The basicity of the catalyst increased with the increase in Mg/Al molar ratio and degree of rehydration. They reported a 96 % conversion of oil to FAME (92 % yield) utilizing the rehydrated hydrotalcite under the reaction conditions: 2 wt. % catalyst loading, 48:1 M/O molar ratio, 60 °C temperature and 8 h time.

Zeng *et al.* [117] reported Mg-Al hydrotalcite with various Mg/Al molar ratio and used them as a heterogeneous catalyst for the transesterification of soybean oil. The hydrotalcite calcined at 773 K and 3:1 Mg to Al molar ratio exhibited the highest catalytic activity with 90.5 % conversion of oil using 1.5 wt. % catalyst loading, 6:1 M/O molar ratio, 65 °C temperature and 4 h time. Recently, Ma *et al.* [118] investigated a heterogeneous catalyst Mg-Al hydrotalcite in the production of biodiesel from WCO. They mentioned that the catalyst with Mg/Al molar ratio 3:1 and calcined at 500 °C have a high surface area, excellent crystallinity and mesoporous structure, subsequently showed excellent activity. They also reported 95.2 % FAME yield under the optimized reaction condition (1.5 wt. % catalyst loading, 6:1 M/O molar ratio, 80 °C temperature and 2.5 h time). In the same manner, Zeng *et al.* [119] prepared Mg/Al-CO_3 with Mg/Al molar ratio of 4:1 *via* urea method and compared their structures and catalytic activities with those prepared by co-precipitation for the biodiesel synthesis from microalgae oil. They studied the crystal size and surface basicity of all the prepared hydrotalcites and reported that the crystal size of the hydrotalcites prepared using urea method is greater than as-synthesized ones. They also reported that the mixed oxide of the hydrotalcite prepared *via* urea method showed the highest catalytic reactivity with the maximum conversion of 90.30 %.

Further, Mg-Al hydrotalcite loaded with 1.5 % K was prepared and used as a catalyst for the synthesis of biodiesel from palm oil [120]. A maximum 86.6 % yield was reported using 7 wt. % catalyst concentration, 30:1 M/O molar ratio, 100 °C temperature and 6 h time. They also studied the effect of the synthesized biodiesel on six types of elastomers such as NBR, HNBR, NBR/PVC, acrylic rubber, co-polymer FKM, and terpolymer FKM, which are commonly found in the fuel system. For testing, the elastomers were immersed in B10 (10 % biodiesel in diesel) and found that only terpolymer FKM and co-polymer FKM showed a slight change in the properties. Thus, concluded that B10 is compatible with the diesel engines without any modification. In another work, Liu *et al.* [121] prepared Zn-Al hydrotalcite within the temperature range of 413-773 K to form dehydrated Zn-Al hydrotalcite and Zn-Al mixed oxides and used both the catalysts in the transesterification reaction in a fixed-bed reactor. The OH groups in the dehydrated Zn-Al is responsible for the high basicity of the catalyst. However, Mn^+-O^{2-} pairs and isolated O^{2-} anions are the main basic sites in Zn-Al metal oxides. Furthermore, they compared the catalytic activity of both dehydrated Zn-Al HT and Zn-Al oxides and found that the dehydrated HT calcined at 473 K showed highest catalytic activity and stability towards biodiesel synthesis with a maximum yield of 76 % at 140 °C for 1 h. Similarly, a heterogeneous base catalyst, KF/Ca-Al was developed for the biodiesel production from palm oil [122]. The catalyst was prepared from layered double hydroxides of Ca-Al, where the introduction of KF enhanced the catalytic activity. It was observed that 100 wt. % loading of KF decreased particle size of catalyst as shown by the SEM image of KF/Ca-Al (Figure 8). The authors also reported biodiesel yield of 97.14 % under the optimized reaction conditions. Besides, biodiesel production from poultry fats was reported by using a solid base catalyst, Mg-Al hydrotalcite [123]. The influence of calcination temperature for the preparation of catalyst was investigated and disclosed that the catalyst calcined at 550 °C showed the maximum catalytic activity. Moreover, the authors detailed that rehydration of the catalyst before the transesterification reaction and preferential adsorption of TAGs on the surface of the catalyst reduced the catalytic activity.

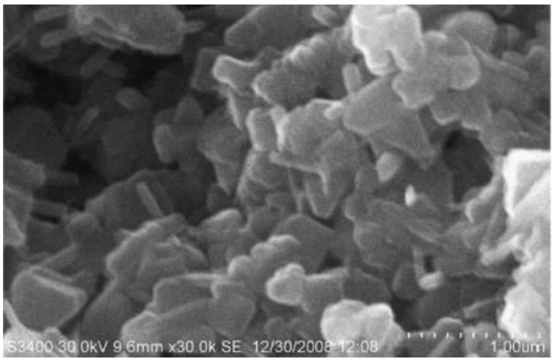


Figure 8: SEM image of KF/Ca-Al. Adapted from ref. [122].

Helwani *et al.* [124] synthesized Mg-Al hydrotalcite *via* combustion method using saccharose for biodiesel synthesis from JCO. SEM image of the catalyst calcined at 850 °C displays a lamellar microstructure with closely packed flakes (Figure 9). The catalyst calcined at 850 °C and recrystallized with 20 % saccharose fuel showed the best reactivity with 75.2 % biodiesel conversion under the optimized reaction conditions. A layered double hydroxide of zinc hydroxide nitrate was also reported for FAME synthesis from palm oil [125]. The catalyst showed excellent reactivity towards the transesterification reaction with 96.5 % biodiesel yield.

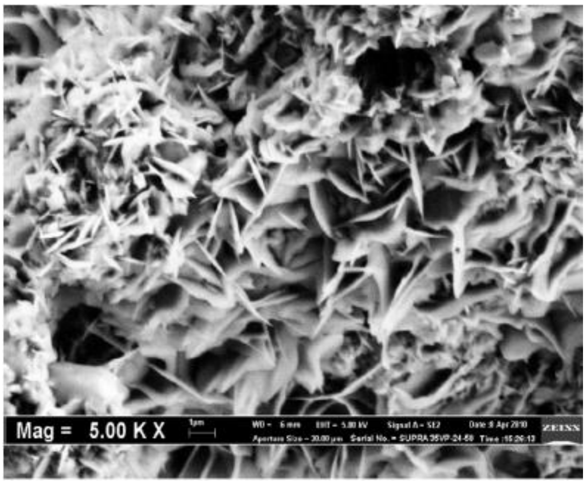


Figure 9: SEM image of Mg-Al HT calcined at 850 °C Adapted from ref. [124].

Table 9: Different hydrotalcite catalyzed FAME production under various reaction conditions.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1	Mg-Al HT	Sunflower oil	48:1, 2, 60, 480	92	[116]
2	Mg-Al HT	Soybean oil	6:1, 1.5, 65, 240	90.5	[117]
3	Mg-Al HT	WCO	6:1, 1.5, 80, 150	95.2	[118]
4	Mg/Al-CO_3	Microalgae oil	6.4:1, 1.7, 66, 240	90.3	[119]
5	K/Mg-Al HT	Palm oil	30:1, 7, 100, 360	86.6	[120]
6	Zn-Al HT	Soybean oil	26:1, NR, 140, 60	76	[121]
7	KF/Ca-Al	Palm oil	12:1, 5, 65, 300	97.98	[122]
8	Mg-Al HT	Poultry fat	30:1, 10, 120, 120	75	[123]
9	Mg-Al HT	Jatropha oil	30:1, 5, 160, 240	93.4	[124]
10	$Zn_5(OH)_8(NO_3)_2 .2H_2O$	Palm oil	6:1, 2, 140, 120	96.5	[125]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).

NR= Not reported

8.1.5 Zeolites

Zeolites are crystalline aluminosilicates that possess microporous structure [126]. Zeolites can exist in different structural morphology depending on their synthesis process and reaction conditions such as Si/Al molar ratio, pour sizes and proton exchange levels. The wide opportunity for structural modification of zeolites makes them an excellent catalyst for various acid-base reactions. Recently, zeolites are intensively investigated in the field of biodiesel production due to their shape selectivity and acidic character. Normally, zeolites are moderately active for the esterification reaction, however, by increasing the pore size and varying the Si/Al ratio, the catalytic properties can be improved. Moreover, zeolites can incorporate various metal ions such as Na^+, K^+, Mg^{2+} etc., which are mainly responsible for its basic nature [127]. Table 10 shows various reported zeolite catalysts employed in biodiesel synthesis.

In 2007, NaX zeolite loaded with various concentration of KOH was synthesized and reported as a catalyst in FAME production from soybean oil [128]. Catalyst loaded with 10 % KOH followed by heating at 393 K for 3 h gave the best result with 85.6 % yield under the optimized reaction conditions. Shu *et al.* [129] prepared La/zeolite beta using $La(NO_3)_3$ as a precursor *via* ion exchange technique and exploited in FAME production from soybean oil. They reported that La/zeolite beta has higher stability and catalytic activity towards FAME production compared to zeolite beta catalyst. A yield of 48.9 % was obtained using La/zeolite beta under the optimized reaction conditions such as 14.5:1 M/O molar ratio, 0.011 wt. % catalyst loading, 60°C and 4 h time. In the year 2008, Ramos *et al.* [130] studied three zeolites such as mordenite, beta and X for the conversion of sunflower oil biodiesel. They examined the effect of different loaded/stacked metals on such zeolites. Zeolite X showed the best catalytic activity as it has a higher number of super basic sites which is absent in other zeolites. Effect of binder, sodium bentonite, on the catalytic reactivity of such zeolites was tested, where X zeolite was agglomerated and thus catalytic activity reduced slightly. A high yield of 93.5 % and 95.1 % of FAME was obtained at 60 °C with and without binder, respectively. In another report, Wu *et al.* [131] **s**ynthesized a series of CaO supported on zeolites such as NaY, KL and NaZSM-5 *via* microwave irradiation and utilized in biodiesel synthesis from soybean oil. They reported that supported CaO showed better result compared to the naked CaO as supported catalyst have a high surface area, porosity and basic strength. Accordingly, the best result was exhibited by NaY supported CaO (30 % CaO loaded on NaY) under the optimized reaction conditions such as 9:1 M/O molar ratio, 3 wt. % catalyst loading, 65 °C and 3 h time.

Strontium nanocatalyst supported on ZSM-5 by incipient wetness impregnation method was prepared and applied in biodiesel synthesis from sunflower oil [132]. The authors reported the effect of calcination temperature and Sr/ZSM-5, Ba-Sr/ZSM-5 mass ratios. Ba-Sr/ZSM-5 (Ba 4 wt. % to the Sr weight and Sr 6 wt. % to the ZSM-5 weight exhibited the best performance with 87.7 % yield under optimal conditions such as 9:1 M/O molar ratio, 60 °C and 3 h time. In the meantime, Narkhede *et al.* [133] synthesized a series of 12-tungstosilicic acid, SiW_{12} (10-40 wt. %) impregnated on zeolite Hβ and applied it in biodiesel synthesis from soybean oil. Interestingly, SEM image of the 30 % SiW_{12}/Hβ (Figure 10b) is similar with the pure zeolite Hβ (Figure 10 a) and revealed that framework structure of Hβ was retained even after the impregnation of SiW_{12} and suggested that SiW_{12} was homogeneously distributed in the framework structure of Hβ zeolite. They reported a 95 % yield of FAME under the optimized reaction conditions.

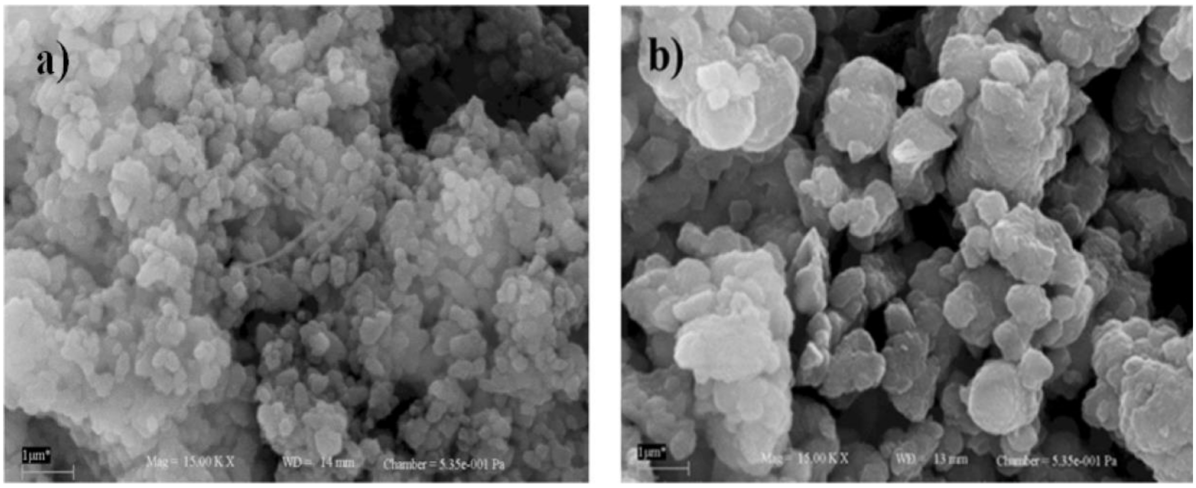


Figure 10: SEM micrographs of (a) Hβ and (b) 30 % SiW_{12}/Hβ. Adapted from ref [133].

In 2012, Babajide *et al.* [134] synthesized a zeolite derived from fly ash and then ion-exchanged with K to form FA/K-X zeolite, which was then applied in biodiesel synthesis from sunflower oil. They reported a high yield of 83.53 % under the optimized reaction conditions such as 6:1 M/O molar ratio, catalyst loading of 3 wt. %, 60 °C temperature and 8 h time. Similarly, Manique *et al.* [135] prepared zeolite (sodalite) derived from coal fly ash *via* the hydrothermal process and utilized in biodiesel synthesis from soybean oil. The developed sodalite has a definite surface area of 10 m^2/g. They also reported a maximum conversion of 95.5 % soybean oil using 12:1 M/O molar ratio, catalyst loading of 4 wt. %, the temperature of 65 °C for 2 h. Recently, Al-Jammal *et al.* [136] prepared zeolite derived from zeolite tuft followed by impregnation of a series of KOH (1-6 M) and heated at 80 °C for 4 h to form

KOH/zeolite catalyst and finally utilized in biodiesel synthesis from waste sunflower oil. The catalyst (1-4 M) KOH/zeolite exhibited a biodiesel yield of 96.7 % under the reaction conditions: 11.5:1 M/O molar ratio, catalyst amount of 6 wt. % w.r.t. oil, 50 °C temperature and reaction time of 2 h.

In the same vein, Du *et al*. [137] developed La_2O_3 impregnated on NaY zeolite catalyst having a spherical shape with 3-5 mm size and utilized it in biodiesel synthesis from castor oil. In addition, they explored the impact of calcination temperature in the range of 600-1000 °C on biodiesel yield and observed that the catalyst calcined at 800 °C showed the best result. They also revealed that the incorporation of surfactant improved the dispersion of La_2O_3 and pore size of zeolite. The XRD pattern of the pure zeolite NaY and the catalyst La_2O_3/NaY zeolite calcined in the temperature range of 600-1000 °C is displayed in Fig.11. The XRD pattern of the pure zeolite (Figure 11 a) and the catalyst calcined at 600 °C (Figure 11b) and 800 °C (Figure 11c) are almost same and revealed that the crystallinity of the zeolite NaY does not change upon the incorporation of La_2O_3. However, on increasing the temperature to 1000 °C, the XRD pattern (Figure 11e) showed no characteristic peaks of zeolite, suggests that at high calcination temperature, the crystallinity of the zeolite is lost.

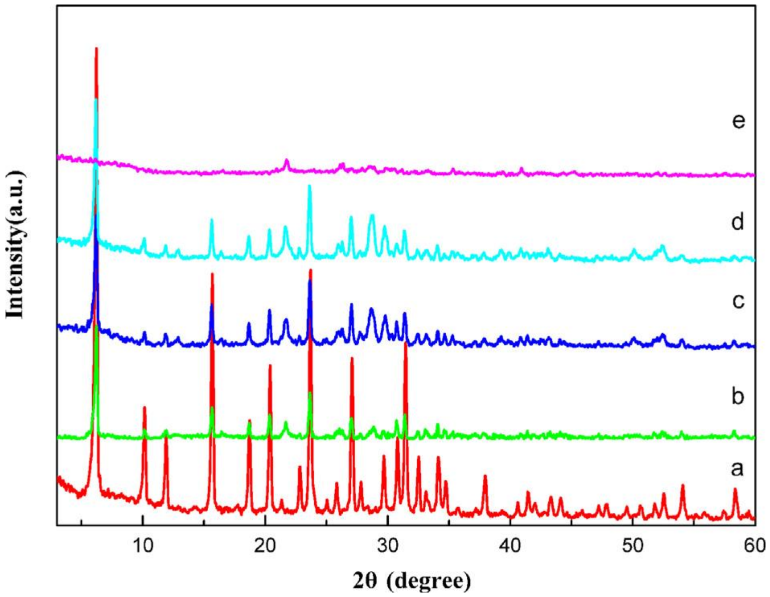


Figure 11: XRD pattern of pure zeolite (a), La_2O_3/NaY-600 (b), La_2O_3/NaY-800 (C), S-La_2O_3/NaY-800 (d), La_2O_3/NaY-1000 (e). Adapted from ref. [137].

Table 10: Different zeolite catalyzed FAME production under various reaction conditions.

No.	Catalyst	Feedstocks	[a]Conditions	Yield (%)	Ref.
1	KOH@NaX zeolite	Soybean oil	10:1, 3, 65, 480	85.6	[128]
2	La/zeolite beta	Soybean oil	14.5:1, 0.011, 60, 240	48.9	[129]
3	Zeolite X	Sunflower oil	6:1, 10, 60, 420	95.1	[130]
4	CaO@NaY zeolite	Soybean oil	9:1, 3, 65, 180	95	[131]
5	Ba-Sr/ZSM-5	Sunflower oil	9:1, 3, 60, 180	87.7	[132]
6	$H_4[W_{12}SiO_{40}]$@zeolite Hβ	Soybean oil	4:1, 0.2, 65, 480	95	[133]
7	FA/K-X zeolite	Sunflower oil	6:1, 3, 60, 480	83.53.	[134]
8	Sodalite	Soybean oil	12:1, 4, 65, 120	95.5	[135]
9	KOH/zeolite	Waste sunflower oil	11.5:1, 6, 50, 120	96.7	[136]
10	La_2O_3/NaY zeolite	Castor oil	15:1, 10, 70, 50	84.6	[137]

[a]Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^oC), reaction time (min).

8.1.6 Supported catalyst

Catalyst support plays an important role in the heterogeneous catalyst as they can reduce the mass transfer limitation and provide a high surface area with high porosity, where metals are anchored [138]. Till now several catalyst support such as alumina, silica, ZnO and ZrO_2 had been proposed for the production of FAME. Alumina is extensively employed as catalyst supports for various basic or acidic compounds exploited as a solid catalyst in esterification/transesterification reactions [139]. Several alumina supported catalysts employed in the transesterification reaction for biodiesel synthesis as shown in Table 11. In 2006, Xie *et al.* [140] investigated the potential of KI loaded on Al_2O_3 support catalyst for biodiesel synthesis from soybean oil. They prepared a series of KI@Al_2O_3 catalysts by changing the KI amount and investigated their catalytic activities. They observed that catalyst loaded with 35 % KI and calcined at 773 K showed highest FAME conversion of 96 % against all other catalysts under the same reaction conditions such as 15:1 M/O molar ratio, catalyst amount of 2.5 % and 8 h reaction time. In another study, potassium oxide loaded on alumina derived from various potassium salts such as KNO_3, KOH, KF, KI and K_2CO_3 were compared and found that KF@Al_2O_3 showed the best result compared to other catalysts, because of the generation of new phase K_2O on the surface of alumina and as result basicity of the catalyst increases [141]. In addition, Ma *et al.* [142] reported the synthesis of FAME via transesterification of rapeseed oil using K@KOH@Al_2O_3 catalyst. The formation of Al-O-K composite enhanced the basicity of the catalyst, thereby catalytic efficiency. They investigated catalytic activity by varying the amount of K and KOH and found that 7.5 and 20 wt. % (w.r.t. alumina) of K and KOH, respectively displayed the highest activity with 84.52 % biodiesel yield. Moreover, Chen *et al.* [143] reported biodiesel production from soybean oil using K@γ-Al_2O_3 catalyst in a rotating packed bed (RPB) reactor. The schematic representation of RPB model is displayed in Figure 12. The main advantage of RPB reactor is that it provides efficient mixing of three immiscible reactants such as oil, methanol and the catalyst. A high yield of 96.4 % was reported using the reaction conditions: 24:1 M/O molar ratio, 10.6 wt. % catalyst amount, and reaction temperature of 60 °C, the reaction time of 60 and 900 rpm.

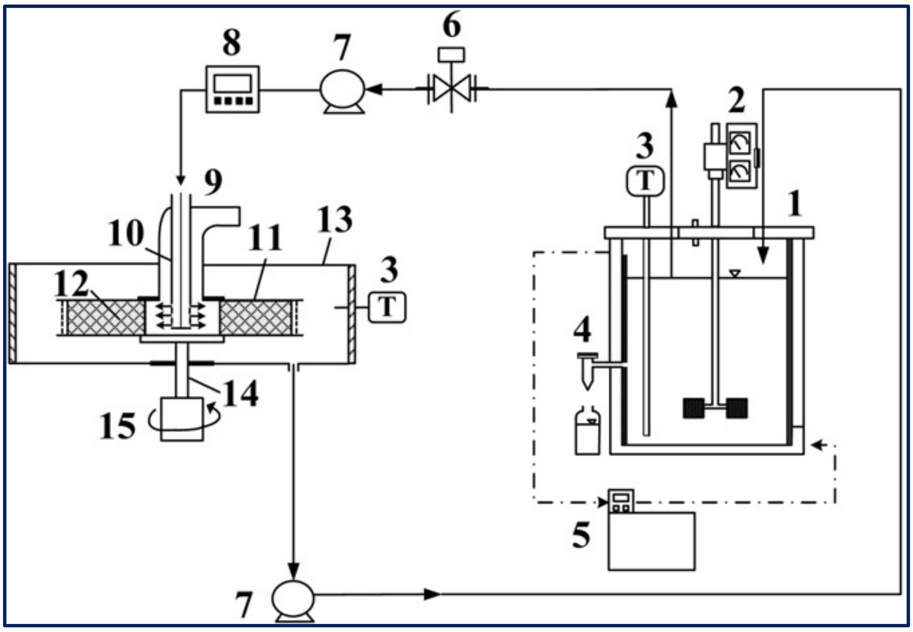


Figure 12: RPB experimental apparatus utilized for heterogeneously catalyzed transesterification reaction. Components: (1) CSTR reactor; (2) stirrer; (3) thermocouples; (4) sample port; (5) thermostat; (6) control valve; (7) pumps; (8) flow-meter; (9) RPB reactor; (10) stationary liquid distributor; (11) packed-bed rotator; (12) K/g-Al2O3 catalyst; (13) housing case; (14) rotor shaft; (15) motor. Adapted from ref. [143].

Zhang *et al.* [144] synthesized KOH impregnated modified alumina catalyst for biodiesel synthesis from microalgae oil. Firstly, the alumina was modified with Lanthanum and barium to increase its surface area, possess desired pore volume and pore distribution and finally impregnation of KOH on the modified alumina to form the desired catalyst. They reported that 25 % KOH (w.r.t. modified alumina) impregnated on modified alumina and calcined at 550 °C for 4 h showed the best activity towards the transesterification reaction with 97.7 % biodiesel yield under the ideal reaction conditions. Umdu *et al.* [145] synthesized $CaO@Al_2O_3$ via the sol-gel method and conducted a transesterification reaction of microalgae (*Nannochloropsis oculata*) oil to produce biodiesel. The catalyst has higher reactivity than the bare CaO, which was almost inactive towards transesterification of the desired microalgae. The alumina was loaded with 80 wt. % (w.r.t. Al_2O_3) $Ca(NO_3)_2.\ 4H_2O$ and calcined at 500 °C for 6 h to form 80 wt. % $CaO@Al_2O_3$ that possessed the highest catalytic activity with 97.5 % biodiesel yield. In addition, Zabeti *et al.* [146] synthesized a $CaO@Al_2O_3$ catalyst using calcium acetate *via* calcination at 718 °C for biodiesel synthesis from palm oil. They have used Response Surface Methodology (RSM) in association with Central Composite Design (CCD) to determine the optimum reaction conditions such as M/O molar ratio, catalyst amount, reaction temperature and reaction time. Biodiesel yield of 98.64 % was obtained under the optimum reaction conditions: 12.14:1 M/O molar ratio, catalyst loading of 5.97 % and temperature of 64.29 °C.

Table 11: Different aluminium supported solid catalyst for biodiesel production.

No.	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1	$KI@Al_2O_3$	Soybean oil	15:1, 2, 65, 480	96	[140]
2	$K@KOH@Al_2O_3$	Rapeseed oil	9:1, 4, 60, 60	84.52	[142]
3	$K@\gamma\text{-}Al_2O_3$	Soybean oil	24:1, 10.6, 60,60	96.4	[143]
4	$KOH/La\text{-}Ba\text{-}Al_2O_3$	Microalgae	NR, 25, 60, 180	97.7^b	[144]
5	$CaO@Al_2O_3$	*Nannochloropsis oculata*	30:1, 2, 50, 240	97.5	[145]
6	$CaO@Al_2O_3$	Palm oil	12:1, 6, 65, 300	98.64	[146]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

^{b}Conversion

NR: Not reported

Apart from alumina, there are several materials which are used as catalyst support such as SiO_2, ZrO_2 and activated carbon (AC) (Table 12). In 2010, Samart *et al.* [147] conducted transesterification reaction using CaO impregnated on mesoporous SiO_2 catalyst for FAME production. They also investigated the influence of CaO amount and reported that 15 wt. % CaO (w.r.t. SiO_2) loading showed the maximum yield of 95.2 %. In addition, the synthesis of FAME from palm oil using a CaO impregnated on bimodal meso-macroporous SiO_2 support catalyst was reported by Witoon *et al.* [148]. They investigated the influence of CaO loading and pellet size on biodiesel conversion and also compared with unimodal SiO_2 supported CaO catalyst. CaO in 40 wt. % CaO@SiO_2 were highly aggregated on the surface of the mesoporous SiO_2, hence increases the surface basicity; while CaO in 30 wt. % CaO@SiO_2 were highly dispersed inside the mesopore of the silica support, accordingly 40 wt. % CaO@SiO_2 showed higher FAME yield compared to 30 wt. % CaO@SiO_2. They also reported that the catalyst with pellet size 335 μm showed a maximum yield of 92.45 %. Moreover, Wu *et al.*[149] reported catalysts consisting of three different potassium compounds (KAc, K_2CO_3 and K_2SiO_3) impregnated on mesoporous SiO_2 such as AlSBA-15 and SBA-15 for the production of FAME from JCO. Three potassium salts with different concentration were impregnated on AlSBA-15 and SBA-15 and found that the basicity lies in the order of 35 wt. % K_2SiO_3@AlSBA-15 > 35 wt. % K_2CO_3@AlSBA-15 > 35 wt. % KAc@AlSBA-15 and thus 30 wt. % K_2SiO_3 showed highest yield of 95.7 % under the reaction conditions: 9:1 M/O molar ratio, the temperature of 60 °C and 3 h time.

The concept of AC-based catalyst is an attempt towards the development of a novel alternative to homogeneous alkaline in the form a heterogeneous catalyst. These kinds of catalysts have pulled in a lot of consideration from the scientific community because the uses of carbon as catalysts not only makes them reusable in the production process but also greatly reduce the formation of the soap and increases glycerol purity [150]. To date, different kinds of activated carbon-based catalysts have been developed and successfully exploited in biodiesel production, some of them are briefly discussed here (Table 18). Narowska *et al.* [150] proposed the development of a novel carbon-based catalyst to replace alkaline homogeneous catalyst as a solid catalyst which has the potential to be reused multiple times, eliminating various limitations associated with other traditional catalysts. In this context, the authors demonstrated the preparation of FAME from corn oil *via* transesterification utilizing KOH supported on activated carbon catalyst. The result showed that the highest yield (92 wt. %) of FAME was recorded using 0.75 wt. % catalyst amount, 1 h reaction time and 3:1 M/O ratio and 62.5 °C reaction temperature. These finding indicated that activated carbon-supported catalysts can be promisingly employed in the transesterification of the waste corn oil using methanol.

Previously, Buasri *et al.* [151] reported calcium oxide impregnated on AC catalyst in the synthesis of highly pure FAME from waste cooking palm oil through continuous transesterification of FFA. After optimization of various reaction, a maximum FAME yield (94 %) was accomplished. In another study, Konwar *et al.* [152] also synthesized AC-supported calcium oxide from *Turbonilla striatula* shell and further, their applicability as a catalyst has been investigated in biodiesel synthesis from vegetable oil. It was observed that more than >90% conversion is possible utilizing this catalyst. Moreover, this approached is economically viable due to easy recoverability of the catalyst. The catalyst was utilized for five progressive reactions cycles with minimum activity loss.

Hameed *et al.* [153] examined a solid catalyst KF supported on AC for biodiesel synthesis from WCO. They designed a composite rotatable reactor to optimize the reaction parameters and obtained 83 % methyl ester yield. In 2010, Baroutian *et al.* [154] studied FAME synthesis in a packed bed membrane reactor (PBMR) from palm oil using a solid catalyst of KOH supported on AC generated from palm shell (Figure 13). They also investigated the impact of reaction parameters using RSM. The highest biodiesel yield of 98.03 % was reported using the catalyst with optimized reaction conditions: 24:1 M/O molar ratio, 64.1 °C temperature and 30.3 wt. % catalyst loading. In addition, Li *et al.* [155] reported in situ synthesis of K_2CO_3@KFA *via* mixing of K_2CO_3 and kraft lignin (KF) succeeded by calcination at 800 °C and utilized the catalyst in biodiesel synthesis from rapeseed oil. They also investigated the influence of reaction parameters on the FAME production and reported that a maximum yield of 99.6 % under the optimized reaction conditions.

Further, Buasri *et al.* [156] conducted a synthesis process where a solution of KOH was mixed with activated carbon (AC) originated from coconut shell to form KOH@AC and used this catalyst in biodiesel synthesis from WCO. The authors claimed that the synthesized catalyst has extraordinary catalytic reactivity and showed 86 % biodiesel yield under the optimized reaction conditions. Similarly, Wan *et al.* [157] examined a solid base catalyst CaO@AC for FAME synthesis from palm oil. RSM was utilized to investigate the impact of reaction parameters on biodiesel synthesis. A maximum yield of 80.98 % was reported under the optimal reaction conditions and also claimed that the catalyst can retain its activity even after two cycles. Recently, Fadhil *et al.* [158] conducted a transesterification reaction of bitter almond oil to produce biodiesel using KAc impregnated on activated carbon originated from the waste of polyethyleneterphathalte. A maximum yield of 93.21 % with high purity was reported. The authors claimed that the catalyst showed excellent reactivity towards biodiesel synthesis compared to other reported solid base catalyst as the catalyst showed a very high yield in very low optimal reaction conditions. Moreover, according to the authors, the catalyst has great stability as it can be reused for 6 cycles.

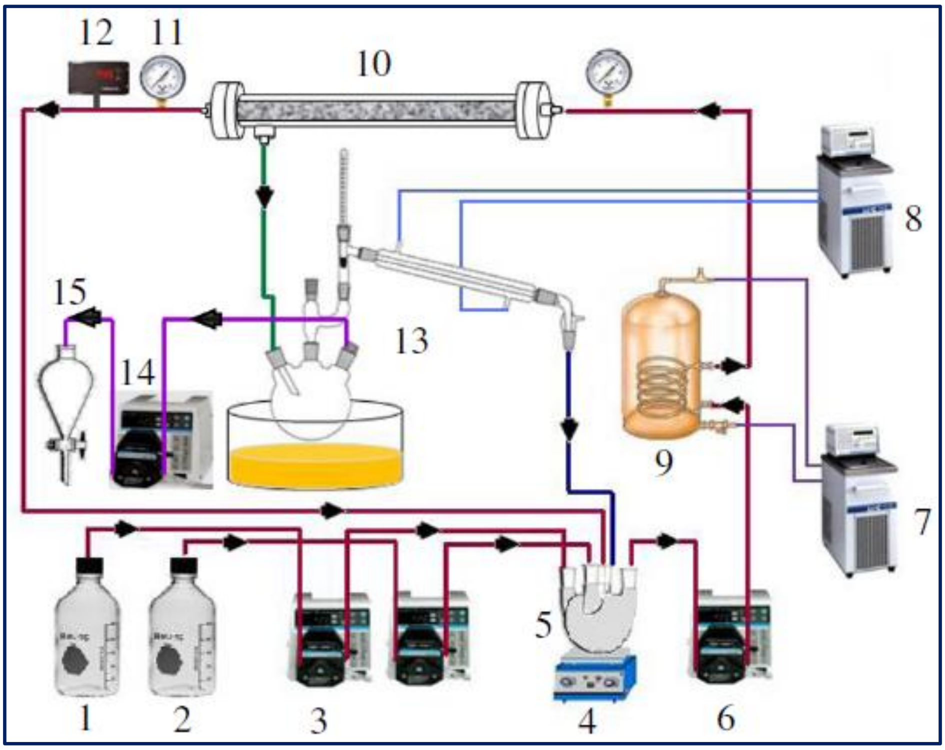


Figure 13: Schematic diagram of PBMR for FAME synthesis. Components: (1) palm oil; (2) methanol; (3) crude material siphon; (4) magnetic stirrer; (5) blending vessel; (6) flowing siphon; (7) boiling water flowing; (8) water chiller; (9) wound thermal exchanger; (10) ceramic membrane; (11) pressure check; (12) temperature indicator; (13) methanol recuperation unit; (14) siphon; (15) isolating funnel. Adapted from ref. [154].

Liu *et al.* [159] examined a solid base catalyst KF/CaO/AC calcined at 500 °C for 5 h for the conversion of soybean oil to biodiesel. The authors claimed that the main catalytic role was played by K_2O and $KCaF_3$ that are present in the catalyst. The catalyst demonstrated high yield of 99.9 % only in 20 min. Nonetheless, they reported that the catalyst is highly sensitive towards water contents in methanol and oleic acid. Therefore it is necessary to use anhydrous oil and methanol to overcome this problem. In conclusion, from all these above-mentioned studies a collective inference can be drawn that activated carbon-based catalysts will be the next generation novel alternative to traditionally available catalysts for efficient transesterification of different oils.

In the meantime, the application of zinc oxide supported silver nanoparticles (ZnO@Ag NPs) as a solid catalyst for the conversion of palm oil to FAME was reported by Laskar *et al.* [160]. The transformation of palm oil to FAME was confirmed using NMR analysis and 10 components of FAME were identified using GC-MS technique, with methyl octadecanoate (C18:0) being the major component. Mixture with different ratio of Ag on ZnO were prepared, where 10 wt. % ZnO@Ag was found to be the most active catalyst producing 96 % FAME under optimum reaction conditions. In the recent past, Taslim *et al.* [161] also demonstrated the efficacy of low-cost AC-based catalyst developed from candlenut shell (an agricultural waste) through the impregnation of KOH for biodiesel production from WCO. The results obtained has shown that the yield of biodiesel up to 96.65 % at a reaction temperature of 60 °C for 2 h, M/O molar ratio of 12:1, and catalyst amount of 3 % can be easily achieved using this catalyst.

Table 12: Different solid supported catalyst for biodiesel synthesis.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1.	CaO/SiO_2	Soybean oil	16:1, 5, 60, 480	95.2	[147]
2.	CaO/SiO_2 (bimodal)	Palm oil	12:1, 5, 60, 240	94.15	[148]
3.	K_2SiO_3@AlSBA-	Jatropha oil	9:1, 15.30, 60, 180	95.7	[149]
4.	KOH/AC	Corn oil	3:1, 0.75, 62.5, 60	92	[150]
5.	CaO/AC	WCO	25:1, NR, 60, 480	94	[151]
6.	CaO/AC	Vegetable oil	40:111,120, 420	>90	[152]
7.					
8.	KF/AC	WCO	8.85:1, 3, 175, 60	83	[153]
9.	KOH/AC	Palm oil	24;1, 30.3, 64.1, 60	98.03	[154]
10.	K_2CO_3@KFA	Rapeseed oil	15:1, 3, 65, 120	99.6	[155]
11.	KOH@AC	WCO	25:1, NR, 60, 120	86.3	[156]
12.	CaO@AC	Palm oil	15:1, 5.5, 190, 81	80.98	[157]

13.	KAc/AC	Bitter almond oil	9:1,2.50, 65, 150	93.21	[158]
14.	KF/CaO/AC	Soybean oil	12:1, 2.1, 65, 20	99.9	[159]
15.	Ag@ZnO	Palm oil	10:1, 10, 60, 60	96	[160]
16.	KOH/AC	WCO	12:1, 3, 60, 120	96.65	[161]

[a] Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).

8.1.7 Biomass-based catalyst

In recent year, bio-waste derived heterogeneous catalyst gains significant attention both in the realm of catalysis and biofuel research, and are reviewed by several authors recently [162],[163],[164],[165],[166],[167]. The advantages of using waste materials as a catalyst are largely due to their cheap, abundant, non-toxic, ecofriendly, economic, renewable, sustainable and easily availability. Many researchers utilized waste biomass as a catalyst for low FFA oil (edible oil) as well as in high FFA oil (edible and non-edible oils). The biomass includes plant ashes, waste shells, bones, industrial wastes and so forth. Profitably, catalysts derived from waste biomass potentially make biodiesel production highly cost-effective and environmentally benign.

8.1.7.1 Ashes of biomass

In recent years, the application of waste plant ashes as a highly active heterogeneous catalyst has drawn increasing attention in the realm of biodiesel production. A huge amount of alkali or alkaline earth elements mostly K, Ca and Mg present in the ashes of waste plant biomass acted as a highly basic catalyst in the transesterification reaction to produce biodiesel from vegetable oil with low FFA. In case of vegetable oil with high FFA, reduction of FFA to <1% (by acid-catalyzed esterification) before transesterification reaction is mandatory to elude catalyst consumption in soap formation, which otherwise leads to low biodiesel yield. Usually, biomass is collected, washed and dried either in oven or sunlight, burnt in the open air or burnt in the air followed by calcination to produce a highly basic ash catalyst as shown in Figure 14. Different basic ash catalysts utilized and their efficacy in the synthesis of biodiesel are presented in Table 13. In a pioneering work, Chouhan *et al.* [168] reported the use of amphibian plant *L. perpusilla* Torrey ash as a solid catalyst in biodiesel synthesis from JCO. The plant biomass was subjected to calcination at 550 ± 5 °C for 2 h to obtain the ash catalyst. The crystallinity of the catalyst was affirmed by XRD patterns. Impact of catalyst loading revealed that 5 wt. % (w.r.t. oil) is enough to obtain a high 89.43% biodiesel yield under the optimal reaction conditions such as molar ratio of M/O as 9:1, 5h reaction rime and 65 ± 5 °C reaction temperature. Nevertheless, reusability study demonstrated that the catalyst lost its reactivity in each progressive reaction cycles owing to leaching of the reactive elements in the catalyst. Thereby, the catalyst was recycled up to 3 cycles only.

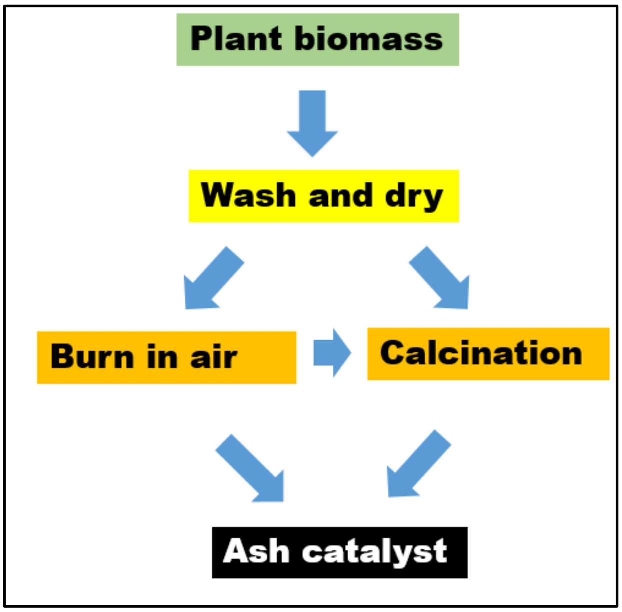


Figure 14: Flowchart for the synthesis of ash catalyst derived from plant biomass.

In another work, oil palm ash was seen as an active catalyst for biodiesel synthesis from WCO by Chin *et al.* [169]. Figure 15 depicted the SEM micrograph of the palm ash, which displayed the porous nature of the ash catalyst, while Table 14 listed the elements exist in the palm ash determined from the EDX analysis. It was observed that the palm ash consisted of a large amount of potassium, while a relatively low quantity of aluminum, zinc, and magnesium was also found. Besides, it was seen that the K_2O was the primary driver for the high basicity and catalytic activity of the catalyst towards biodiesel synthesis. CCD was utilized to investigate the impact of the optimized reaction conditions in biodiesel synthesis such as M/O ratio, reaction time and temperature and catalyst loading. Accordingly, the predicted and experimental biodiesel yields were found to be 60.07 % and 71.74 % respectively.

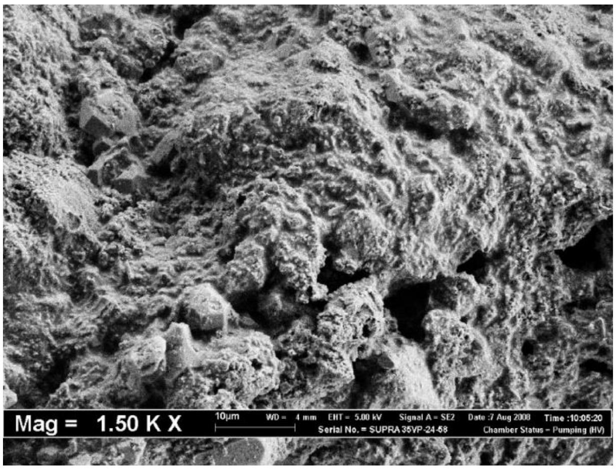


Figure 15: SEM micrograph of palm ash. Adapted from ref [169].

Table 14. EDX data for compositions of palm ash by. Ref. [169].

Elements	Atomic wt. %
Potassium (K)	40.59
Magnesium (Mg)	0.76
Silicone (Si)	2.63
Aluminum (Al)	0.50
Zinc (Zn)	0.33
Oxygen (O)	29.36
Carbon (C)	14.56
Chlorine (Cl)	7.07

In the meantime, Boey *et al.* [170] reported a solid base, derived from boiler ash (BA) *via* calcination, catalyzed biodiesel synthesis from palm oil. BA effectively transformed palm oil to FAME at moderate reaction conditions (3 wt. % catalyst loading, M/O molar ratio of 15:1, 60 °C and 30 min reaction temperature and reaction time respectively) and delivered 90% FAME yield. Ironically, the ash is intolerant to the presence of moisture and FFA at 1 wt. % in the feedstock. Betiku *et al.* [171] reported a process for biodiesel synthesis from *Thevetia peruviana* oil by utilizing calcined *Musa paradisiacal* (plantain) peel ash catalyst. The dried powdered plantain peels were calcined at 500 °C for 3.5 h to produce plantain peels ash. Biodiesel yield of 95.2% was acquired using the optimized reaction conditions: catalyst loading of 3 wt. %, M/O molar ratio of 3.3/1, reaction temperature and time of 60 °C and 60 min. In addition, Etim *et al.* [172] utilized ripe plantain fruit peel as a solid catalyst in biodiesel synthesis from *Azadirachta indica* oil. At the onset, pre-esterification of the oil was performed to diminish the FFA contents from 5.81 wt. % to 0.90 wt. % utilizing M/O molar ratio of 2.19 v/v and 6 wt. % of $Fe_2(SO_4)_3$. Finally, the pre-esterified oil was transformed to FAME *via* transesterification reaction catalyzed by plantain fruit peel ash. Coconut husk ash catalyst was also reported for biodiesel synthesis from JCO [173]. The husks were subjected to calcination at various temperatures ranging from 250-500 °C and identified that catalyst produced at 350 °C calcination temperature was found to be the most reactive one for biodiesel synthesis giving 99.86 % yield within 30 min at the moderate reaction temperature. XRD patterns of the catalysts are presented in Figure 16 which revealed the presence of several components of ash such as KCl, $K_2Si_2O_5$, K_2SO_4, K_2S_3, $KAlO_2$, $K_4CaSi_3O_9$, $FeCa_2Al_2BSi_4O_{15}OH$, etc.

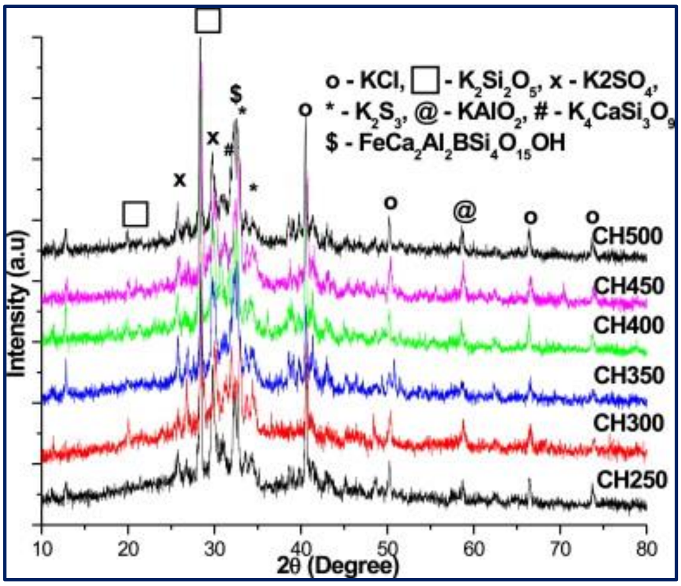


Figure 16: XRD patterns of calcined coconut husk calcined at different temperatures. Adapted from ref [173].

Cocoa pod husks (CPHs) was used as a solid catalyst for biodiesel synthesis from soybean oil by Ofori-Boateng *et al.* [174]. The authors examined the reactivity of MgO impregnated CPH (MgO@CPH) and bare CPH in biodiesel synthesis under the optimal reaction states: for MgO@CPH (M/O ratio of 6:1, 1 wt. % doped MgO@CPH, 60 °C and 60 min) and CPH (M/O ratio of 6:1, 60 °C, 120 min, 1 wt. % catalyst), and achieved 98.7% and 91.4% biodiesel yields respectively. Moreover, the synthesized fuel satisfies the European biodiesel quality norm (EN 14112). In another study, the production of biodiesel from yellow oleander (*Thevetia peruviana*) seed oil using banana (*Musa balbisiana* Colla) peel ash was reported [175]. K, Na, CO_3, Cl present in the ash are responsible for the high basicity, thus the reactivity of the catalyst. Oil transformation of 96 % was demonstrated in just 3 h time under room temperature. The produced biodiesel conform to standards set for ASTM D6751, EN 14214 and so forth. BET surface area measurement of the catalyst revealed that the surface area is 1.487m^2/g. The biodiesel was free from sulfur and has displayed a high cetane number. Meanwhile, *Musa balbisiana* Colla underground stem (MBCUS) ash was examined as a solid base catalyst for biodiesel synthesis from high FFA containing JCO by Sharma *et al.* [176]. Characterization of the ash catalyst revealed that it is comprised of oxides and carbonates of various alkali and alkaline earth metals, which leads to the high basicity of the catalyst and surface area is 39 m^2/g. It was reported that the catalyst is very effective during the biodiesel synthesis process at 275 °C and internal pressure (4.2 MPa) and resulted in 98.0 % biodiesel yield.

Betiku *et al.* [177] led an investigation on the application of banana (Musa‘Gross Michel’) peel waste as a catalyst for biodiesel synthesis from *Bauhinia monandra* (Napoleon's plume) seed oil (BMSO), with a motive to develop a low-cost fuel. The burnt ash of the banana peel was further calcined at 700 °C for 4 h to produce a highly active catalyst. They have utilized RSM model to determine the optimal reaction conditions for biodiesel synthesis using the ash catalyst. The RSM plot of M/O molar ratio and catalyst loading on *Bauhinia monandra* (Napoleon's plume) methyl ester (BMME) yield is shown in Figure 17a. It is observed that BMME yield improved from 0 to >90 wt. % as the M/O molar ratio expanded from 7:1 to 14:1 and catalyst loading increased from 1.5 to 3.5 wt. %. This might be ascribed to the increase in active sites number as a result of increased in catalyst loading. Besides, BMME yield diminished marginally when the catalyst loading was above 3.5 wt. % (Figure 17a). In addition, the plot revealed a direct connection between the M/O molar ratio and catalyst loading on the biodiesel yield. As the two parameters increases, biodiesel yield also increased (Figure 17a). The transformation of the pre-esterified oil to biodiesel was done inside the time span of 33.79-76.21 min. The extended reaction time, somewhere in the range of 33.79 and 55 min, favoured biodiesel yield; after 55 min, the yield diminished. Figure 17b displays the impact of reaction time and catalyst loading on biodiesel yield. It is observed from the surface plot that rise in catalyst loading and reaction time leads to an increase in biodiesel yield. Moreover, the plot displayed that 90 wt. % biodiesel yield is reached using 4.5 wt. % catalyst loading within 80 min reaction time. In addition, Figure 17c illustrates the surface plot to examine the impact of M/O molar ratio and reaction time on biodiesel yield. It is observed from the plot that increases in two parameters such as M/O molar ratio and reaction time leads to a rise in biodiesel yield. It is seen from the figure that increases in M/O molar ratio from 7:1-14:1 improved the biodiesel yield from 33% to 100 %. Therefore, the highest biodiesel yield was recorded at 14:1 M/O molar ratio and 80 min reaction time.

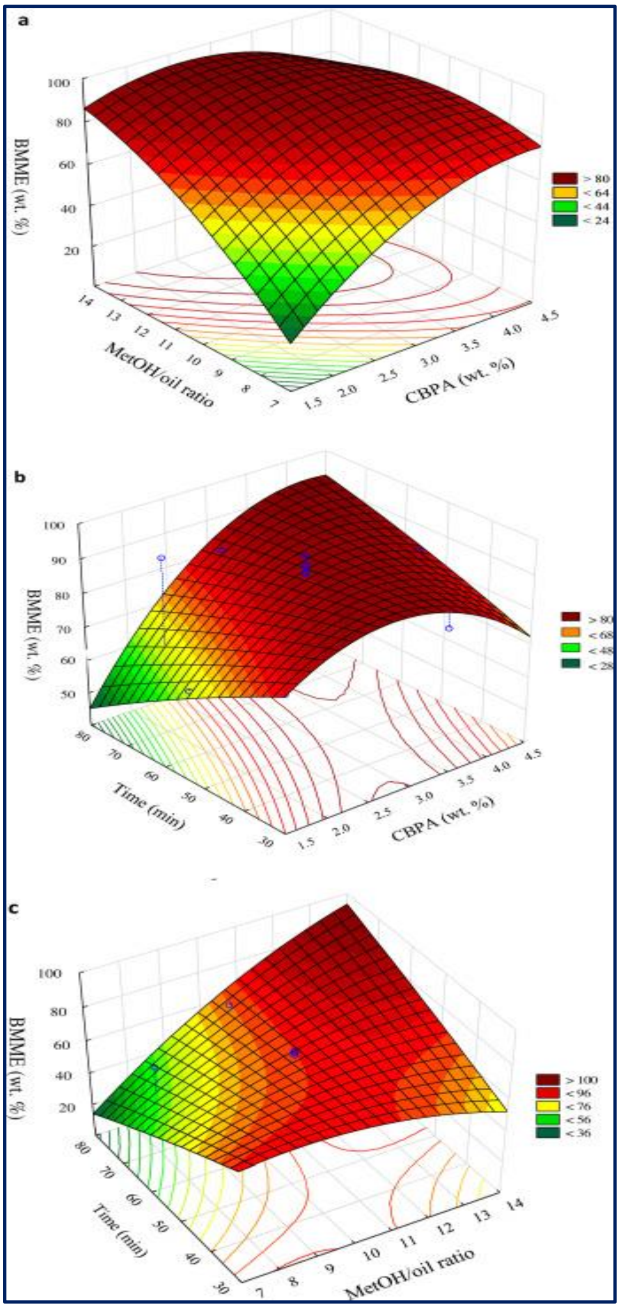


Figure 17: 3-D plots of biodiesel yield. Adapted from ref. [177].

Meanwhile, Onoji *et al.* [178] built up a novel technique to utilize rubber seed shell (RSS) ash calcined at 800 °C as a solid base catalyst for the transformation of rubber seed oil to biodiesel. The high FFA content of the RSS (9.01 ±0.07%) was pre-esterified using H_2SO_4 to >1% FFA. Reusability study of the catalyst revealed that >80 % biodiesel yield was noticed after 4 successive reaction cycles. The surface area and pore size of the calcined RSS was found to be 2.29 nm and 352.51 m^2/g, respectively. Similarly, Gohain *et al.* [179] studied the application of *Musa balbisiana* Colla peel ash catalyst to produce biodiesel from WCO. It was observed that the calcination procedure improved the mesoporous and microporous morphology of the catalyst and upgraded its surface area bringing about the higher catalytic activity. The external morphology of the catalyst examined by SEM analysis revealed aggregation of the particles and porosity in the range of micro and meso. Moreover, 100 % conversion of WCO to biodiesel was confirmed by ^1H NMR spectra (Figure 18b) utilizing Knothe and Kenar equation (1). The ^1H NMR spectrum of WCO (Figure 18a) displays two peaks at 4.1 and 5.3 ppm because of the glyceridic protons (Figure 18a). The presence of peak of methoxy protons at ∼3.6 ppm and vanishing of the signs of glyceridic peak close to 4-4.2 ppm (Figure 18b) confirmed the formation of biodiesel.

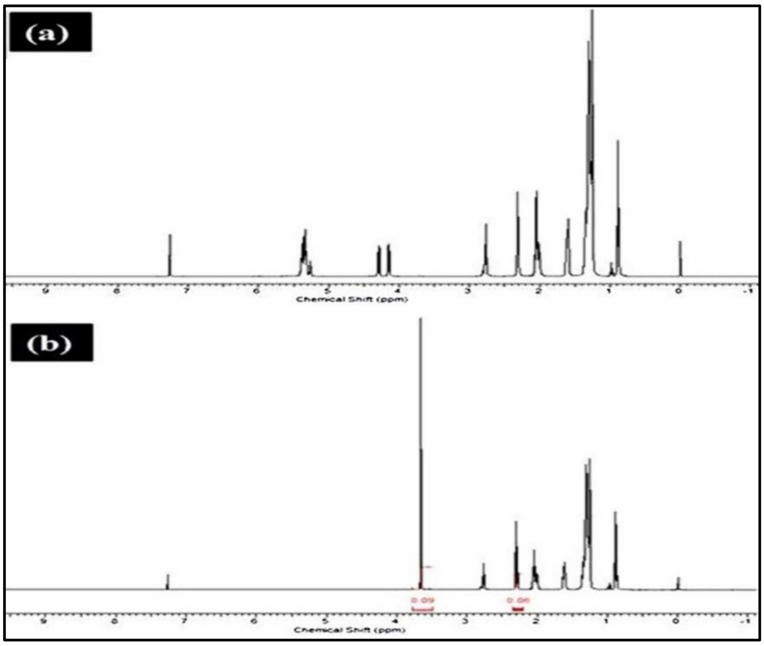


Figure 18: ^1H NMR Spectrum of (a) WCO and (b) Biodiesel. Adapted from ref. [179].

In the recent year, Pathak *et al.* [180] utilized *Musa acuminata* peel ash (MAPA) catalyst for biodiesel synthesis from soybean oil at room temperature. Catalyst characterization reported the existence of various alkali and alkaline earth metals that enhance the catalyst basicity and reactivity of the ash catalyst. The SEM and TEM analysis revealed the porous nature of the catalyst which may be an explanation behind its high catalytic reactivity (Figure 19). K (14.27 %), C (47.51 %) and O (30.27 %) are the primary/main elements exist in MAPA as revealed by the XPS data (Figure 20). The authors reported 98.95 % biodiesel yield under the optimized reaction conditions of M/O molar ratio of 6:1, catalyst loading of 0.7 wt. %, the reaction time of 4 h.

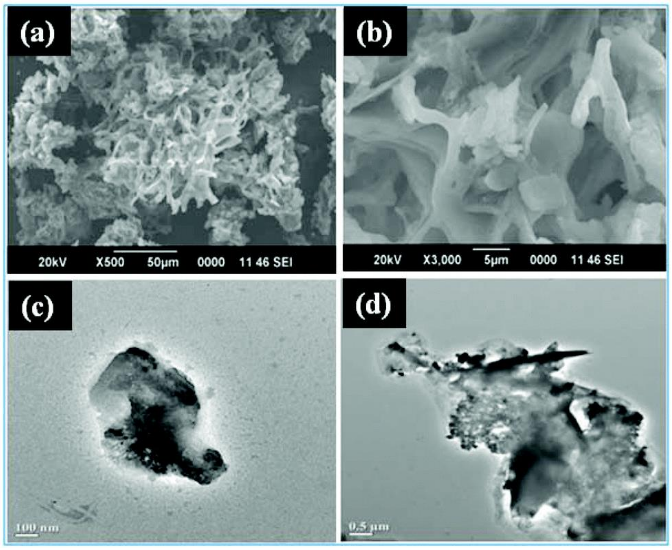


Figure 19: SEM micrographs (a, b) and TEM micrographs (c, d) of MAPA. Adapted from ref. [180].

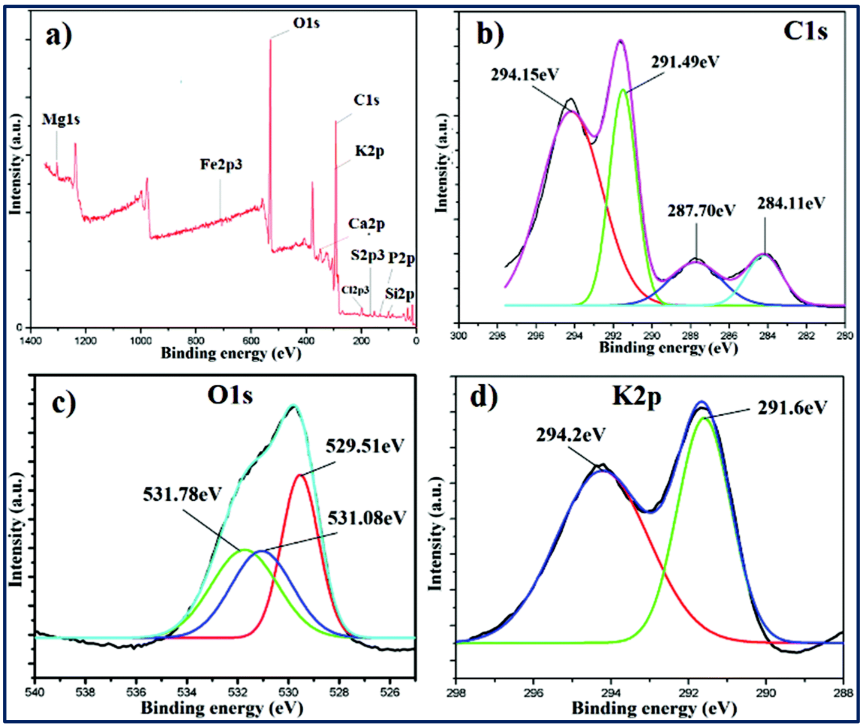
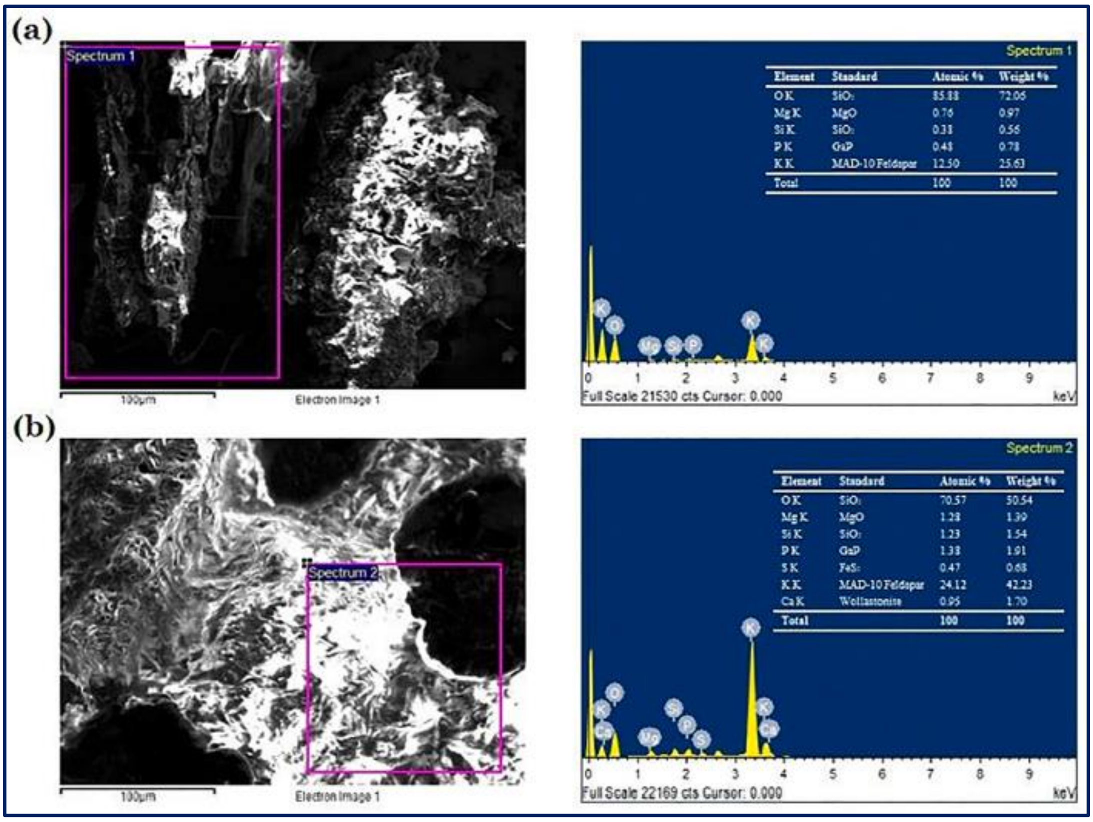


Figure 20: XPS survey (a), C 1s (b), O 1s (c), and K 2p (d) spectra of MAPA. Adapted from ref. [180].

Sharma *et al.* [181] investigated the reactivity of wood ash catalyst calcined at different temperature for biodiesel synthesis from JCO. Ester conversion in the range of 97-99% could be achieved with wood ash catalysts. Wood ash calcined at 800 °C afforded 98.7% oil conversion under the ideal reaction conditions. Uprety *et al.* [182] studied the application of wood ash derived from birch bark and fly ash blazed at 800 °C for 4 h synthesis of biodiesel from palm oil. Birch bark ash gave FAME yield of 88.06 ± 0.72, whereas, fly ash from wood pellet afforded 99.92 ± 0.01% yield. Recently, the application of banana peduncle ash as an efficient solid base catalyst for the synthesis of biodiesel from *Ceiba pentandra* oil (CPO) was investigated [183] investigated. Based on the response surface methodology (RSM) study, the ideal reaction conditions for the transformation of CPO into FAME was found to be 1.978 wt. % catalyst loading, 60 min response time, 9.20:1 M/O molar ratio with a maximum predicted FAME yield of 99.36 % which was assessed experimentally as 98.69 ± 0.18%. The same research team also investigated the utilization of *Musa acuminata* peduncle for biodiesel preparation from CPO [184]. The authors calculated the surface area and pore diameter of the calcined ash catalyst from BET analysis data and reported 45.99 m^2/g and 9.77 nm respectively. Moreover, the catalyst consists of diverse minerals along with potassium as primary components, which leads to the higher reactivity of the catalyst (Figure 21). High conversion of 98.73 ± 0.50 % FAME was observed under the optimum reaction conditions.



Spectrum 1

Element	Standard	Atomic %	Weight %
O K	SiO_2	85.88	72.06
Mg K	MgO	0.76	0.97
Si K	SiO_2	0.33	0.56
P K	GaP	0.48	0.78
K K	MAD-10 Feldspar	12.50	25.63
Total		100	100

Spectrum 2

Element	Standard	Atomic %	Weight %
O K	SiO_2	70.57	50.54
Mg K	MgO	1.28	1.39
Si K	SiO_2	1.23	1.54
P K	GaP	1.38	1.91
S K	FeS_2	0.47	0.68
K K	MAD-10 Feldspar	24.12	42.23
Ca K	Wollastonite	0.95	1.70
Total		100	100

Figure 21: EDS images (a) uncalcined and b) calcined banana peduncle. Adapted from ref. [184].

In 2019, Mendonça *et al.* [185] reported the utilization of calcined (800 °C for 4 h) waste cupuaçu seeds as a solid base catalyst in the synthesis of biodiesel from soybean oil and ethanol. Ideal procedure (catalyst loading of 10% (w/w), 10:1 ethanol/oil molar ratio, reaction time 8 h, and temperature 80 °C) brought about oil transformation of 98.36 %. Similarly, Nath *et al.* [186] utilized a solid base catalyst derived from waste *Brassica nigra* plant for the efficient preparation of biodiesel. The SEM-EDX analysis of the catalyst revealed the existence of potassium (56.13 %) and calcium (26.04 %) in huge amount, which may be considered as key ingredients for the high basicity of the catalyst. The authors also measured the surface area pore volume of the catalyst *via* BET analysis and came about 7.308 m^2/g and 0.011 cm^3/g respectively. The catalyst possessed excellent reactivity in transforming the soybean oil to FAME and displayed 98.79% FAME yield in a short time frame of 25 min under the optimum states: 12:1 of M/O ratio, 7 wt. % of catalyst loading and 65 °C temperature. Betiku *et al*. [163] prepared ash catalyst from kola nut pod husk and used it to convert Kariya seed oil (KSO) to biodiesel, namely Kariya oil methyl esters (KOME), via transesterification process. A maximum of 98.67 ± 0.01 wt. % of FAME yield was observed. Moreover, the reusability examination of the catalyst suggests that it can be reused for 4 progressive cycles. Recently Changmai *et al.* [187] converted soybean oil to biodiesel using orange peel ash in 98 % yield. XRF analysis showed the presence of oxide of potassium (51.64 %) and calcium. Hammet indicator strategy was employed to examine the catalyst basicity and it was seen as $9.8< H\_<12.2$. The author's measured catalyst pore volume and surface area from BET analysis and found 0.428 cc/g and 605.60 m^2/g, respectively. Moreover, GC-MS analysis reveals the existence of six components in the synthesized FAME; methyl palmitate (11.63 %), methyl oleate (25.32 %) and methyl linoleate (54.34 %) are the major components.

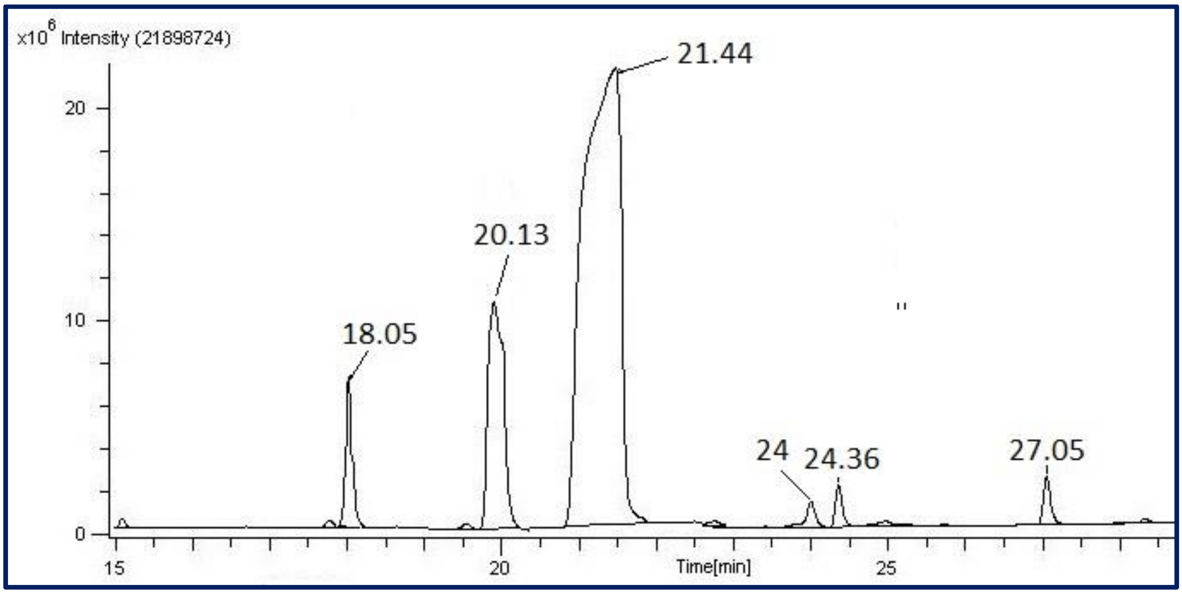


Figure 22: GC-MS spectrum of biodiesel from soybean oil. Adapted from ref. [187].

Waste *Sesamum indicum* plant ash catalyst was also successfully utilized for the transformation of sunflower oil to biodiesel [188]. The measured surface area of the catalyst is 3.66 m^2/g as obtained from the BET analysis data. A high 98.9 % biodiesel yield was accomplished. They reused the catalyst up to the 3rd cycle which yields 94.2 % biodiesel. In addition, Mendonça *et al.* [189] utilized waste tucumã peels ash catalysts for biodiesel synthesis from soybean oil. The catalyst characterization by XRF showed it was mostly composed of oxides of potassium, calcium and magnesium. The reaction parameters for transformation reaction of oil optimized at 1 % w/w of the catalyst, 4 h reaction time, 80 °C, and 15:1 M /O molar ratio, afforded high oil conversion (97.3 %). Because of its heterogeneous and non-leachable nature, the catalyst derived from *tucumã* peels could be reused at least 5 times. In another study, *Tectona grandis* leaves ash catalyst was developed and utilized for the transformation of WCO to FAME by Gohain *et al.* [190]. The measured surface area and pore size of the catalyst are 116.833 m^2/g and 112.210 Å, respectively as calculated from BET data. 100 % oil transformation to FAME was accomplished at room temperature utilizing 2.5 wt. % catalyst loading and 6:1 M/O molar ratio and reaction time of 3 h. Furthermore, cocoa pod husk derived solid base catalyst was employed in the transformation of neem seed oil to FAME [191]. A two-step process was employed for the conversion of neem seed oil to FAME, i) pretreatment of the oil was performed using $Fe_2(SO_4)_3$ catalyst to reduce the FFA content from 28.76 % to 0.39 % and ii) transesterification of pretreated oil using the calcined bio waste-derived catalyst. The authors also studied the effect of reaction parameters using Box-Behnken design (BBD) and CCD of RSM was utilized and revealed that 0.73 (v/v) M/O molar ratio, 0.65 (w/v) of catalyst loading, 65 °C temperature and 57 min time showed the maximum yield of 99.3 %. Similarly, a walnut shell derived catalyst was developed for the transformation of sunflower oil to biodiesel [192]. The catalyst was prepared from walnut shells *via* air combustion, thereby bringing down the cost involved in the calcination process to afford ash. The authors reported a 98 % FAME yield within a brief time frame of 10 min. Recently, the transformation of sunflower oil to synthesize FAME using calcined sugar beet generated from agro-industry waste was reported [193]. The catalyst has a high amount of highly basic CaO and showed very high reactivity towards the transesterification process to afford about 93 % FAME yield. 98.39 % soybean oil transformation to FAME under room temperature was reported using *M. acuminata* trunk ash catalyst recently [194].

Most biomass ash catalysts are usually applied for transesterification reactions of different biodiesel feedstocks and different reaction conditions. These make a comparison of the effectiveness of such catalysts under the same reaction condition impossible. Hence, to have a better insight into the activities of catalysts under the same reaction conditions and feedstock, Odude *et al*. [195] examined the transformation of pre-esterified palm kernel oil (PKO) to FAME utilizing two diverse catalysts viz. calcined banana peel ash (CBPA) and calcined cocoa pod husk ash (CCPHA) under same reaction conditions. RSM technique was utilized for the optimization of both CBPA and CCPHA catalyzed transformation process of PKO to FAME. CCD was utilized to acquire the best possible combination of M/O ratio, catalyst loading and reaction time for the highest conversion of oil to FAME as portrayed in Figure 23. The optimal condition such as M/O ratio of 0.80 v/v, 4 wt. % catalyst, the temperature of 65 °C and time of 65 min obtained for both biowaste catalyzed transesterification reactions showed that both catalysts could be used to produce FAME (>99 wt. %). The observed FAME yields under the optimized conditions utilizing catalysts CBPA and CCPHA were 99.5 and 99.3 wt. %, respectively. The created models when exposed to statistical assessment demonstrated that CBPA catalyzed transformation model was better than CCPHA-catalyzed transformation model. In the meantime, *Carica papaya* stem [196] and *Musa balbisiana* underground stem [197] was also reported as a solid catalyst to convert *Scenedesmus obliquus and Mesua ferrea* oil respectively, to FAME.

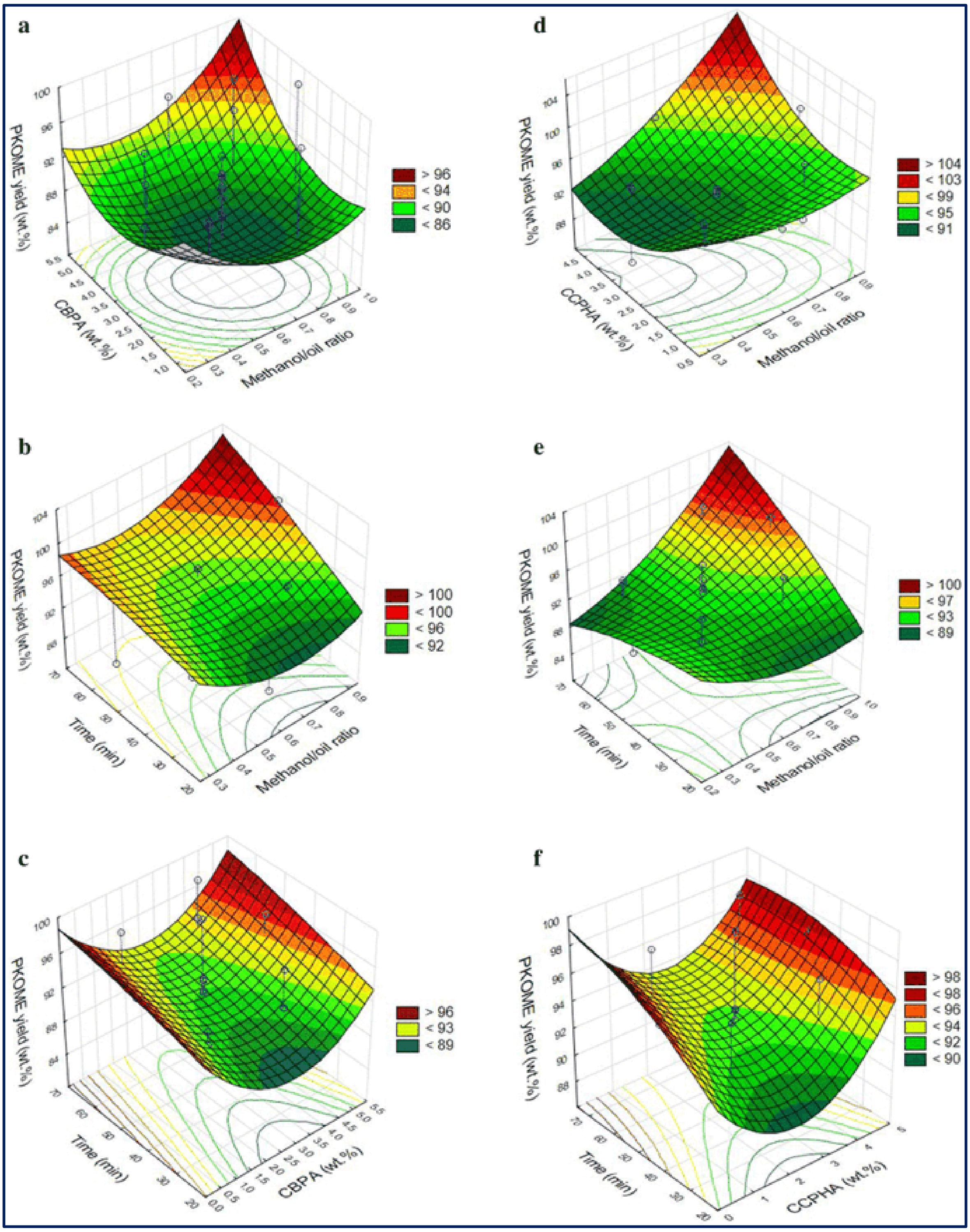


Figure 23: Contour and surface plots for PKOME synthesis. Adapted from ref. [195].

Table 13: Different plant ash catalysts in biodiesel productions

No.	Catalyst source	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	*L. perpusilla* Torrey	JCO	9:1, 5, 65 ± 5, 300	89.43	[168]
2.	Oil palm ash	WCO	18:0, 5.35, 60, 30	71.74	[169]
3.	Oil palm ash/ boiler ash (BA)	Palm olein	15:1, 3, 60, 30	90	[170]
4.	*Musa paradisiacal* (plantain) peels	*Thevetia peruviana* oil	3.3:1, 3, 60, 60	95.2	[171]
5.	Ripe plantain fruit peel	*Azadirachta indica* oil	1:0.73, 0.65, 65, 57	99.2	[172]
6.	Coconut husk	JCO	12:1, 7, 45, 30 min,	99.86	[173].
7.	Cocoa pod husks	Soybean oil	6:1, 1, 60, 60/120	98.7/ 91.4	[174]
8.	*Musa balbisiana* Colla peel	*Thevetia peruviana* seed oil	20:1^d, 20, RT, 180	96^b	[175]
9.	*Musa balbisiana* Colla underground stem	JCO	9:1, 5, 275, 60	98	[176]
10.	Musa'Gross Michel' peel	Napoleon's plume seed oil	7.6:1, 2.75, 65, 69.02	98.5	[177]
11.	Rubber seed shell	Rubber seed oil	0.20:1^e, 2.2, 60, 60	83.06	[178]
12.	*Musa balbisiana* Colla peel	WCO	6:1, 2, 60, 180	100^b	[179]
13.	*M. acuminata* peel	Soybean	6:1, 7, RT, 240	98.95	[180]
14.	Wood (*Acacia nilotica*) stem	JCO	12:1, 5, 65, 180	98.7^b	[181]
15.	Birch bark/ fly ash	Palm oil	12:1, 3, 60, 180	88.06 ± 0.72/ 99.92 ± 0.01	[182]
16.	Musa spp "Pisang Awak" peduncle	*Ceiba pentandra* oil	9.20:1, 1.978, 65, 60	98.69 ± 0.18	[183]

17.	*Musa acuminata* peduncle	*Ceiba pentandra* oil	11.46:1, 2.68, 65, 106	98.73±0.50[b]	[184]
18.	*Theobroma grandiflorum* seeds	Soybean oil	10:1, 10, 80, 480	98.36[b]	[185]
19.	*Brassica nigra* plant	Soybean oil	12:1, 7, 65, 25	98.79	[186]
20.	Kola nut pod husk	Kariya seed oil (KSO)	6:1, 3, 65, 75	98.67±0.01	[163]
21.	Orange peel	Soybean oil	6:1, 7, RT, 420	98[b]	[187]
22.	*Sesamum indicum* plant	Sunflower oil	12:1, 7, 65, 40	98.9	[188]
23.	Tucumã peels	Soybean oil	15:1, 1, 80, 240	97.3[b]	[189]
24.	*Tectona grandis* leaves	WCO	6:1, 2.5, RT, 180	100[b]	[190]
25.	Cocoa pod husk	*Azadirachta indica* oil	0.73:1[e], 0.65, 65, 57	99.3	[191]
26.	Walnut shell	Soybean oil	12:1, 5, 60, 10	98	[192]
27.	Sugar beet waste	Sunflower oil	4.5:1, 1, 75, 60	93[b]	[193]
28.	*M. acuminata* trunk	Soybean oil	6:1, 14, RT, 360	98.39[b]	[194]
29.	Banana peel/ cocoa pod husk	Palm kernel oil	0.80:1[e], 4, 65, 65	99.5/99.3	[195]
30.	*Carica papaya* stem	*Scenedesmus obliquus*	9:1, 2, 60, 180	93.33[b]	[196]
31.	*Musa balbisiana* underground stem	*Mesua ferrea* oil	9:1, 5, 60, 275	95[b]	[197]

[a*] Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).

[b] Conversion

[d] mL/g

[e] v/v.

8.1.7.2 Waste shells

Despite several chemically synthesized heterogeneous catalysts mentioned earlier show promising and comparatively high biodiesel yield, their synthesis routes are sometimes complicated, expensive, chemically wasteful, time consuming and non-economical. Therefore, with the growing high demand for renewable energy, there is a need to search for an ideal heterogeneous catalyst which is easy to synthesize, non-toxic, low cost, widely available, biodegradable and eco-friendly in nature, yet exhibits high catalytic activity in biodiesel production. In the light of this, utilization of CaO (derived from high-temperature calcination of waste shells containing $CaCO_3$) has been a front runner in recent times. The use of waste shells as a source of CaO not only make the whole production of biodiesel sustainable but also solved the problem associated with waste disposal of huge quantities of waste shell generated due to human consumption.

8.1.7.2.1 Eggshell

Various eggshell derived heterogeneous catalysts are available for the transformation of edible/non-edible oils to FAME as listed in Table 15. For the first time, CaO originated from chicken eggshell calcined at 1000 °C was utilized for biodiesel synthesis by Wei *et al.* [198]. Biodiesel yield greater than 95 % was obtained. They have calcined the eggshell at different temperatures from 200 °C to 1000 °C and then tested their efficacy for the transformation of soybean oil to FAME. They observed that those calcined above 800 °C were the most active catalysts, where the XRD spectra display a crystalline CaO (Figure 24). Samples calcined at 700 °C for 2 h contain $CaCO_3$ as the principal constituent and CaO as a minor one, hence medium yield (90 %) were obtained. Calcinations below 600 °C did not result in the formation of CaO, hence, low catalytic activity was observed (<30 % biodiesel yield). Hence, CaO in the catalyst is the principal basic constituent, which led to the high reactivity of the catalyst. From this experiment, it is suggested that waste shells have to be calcined at a temperature of at least 800 °C for 2 h to fully convert $CaCO_3$ to CaO, a highly basic catalyst.

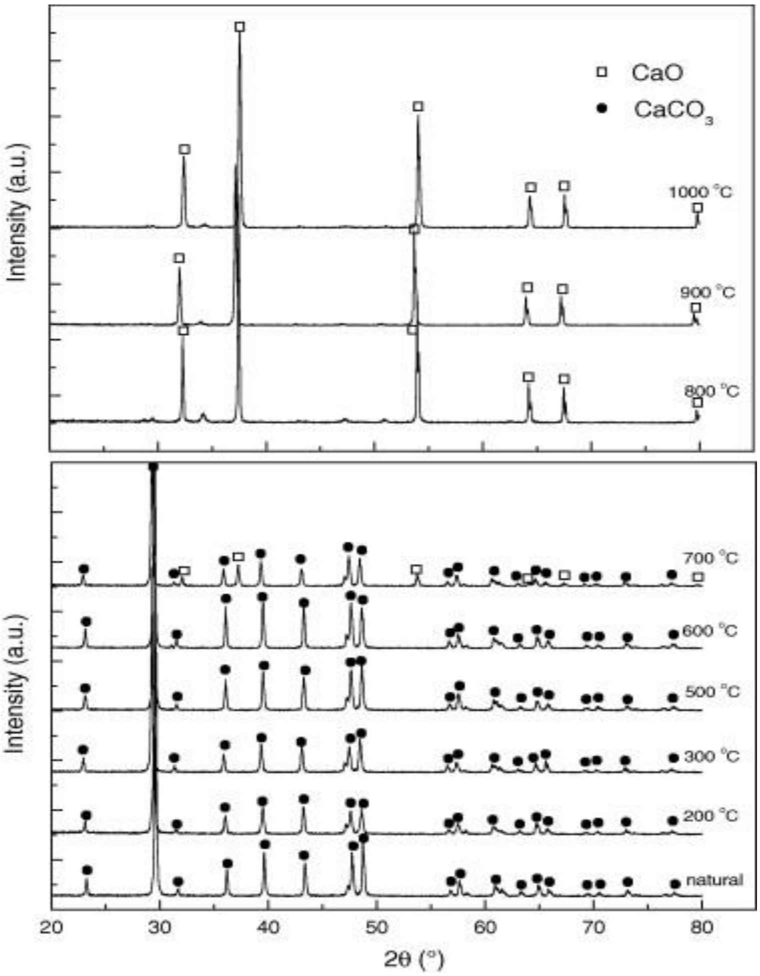


Figure 24: XRD patterns of natural eggshell and the materials obtained by calcining natural eggshell in the range of 200 °C–1000 °C. Adapted from ref.[198].

In recent years, CaO derived from eggshell has been widely investigated in transformation of various edible/non-edible oils such as soybean oil [199],[200],[201] karanja oil [202], WCO [203],[204],[205],[206],[207],[208],[209],[210],[211],[212],[213], palm oil [214],[215],[216],[217], rapeseed oil [218],[219], sunflower oil [220], [221],[222],[223], JCO [224], microalgae oil [225],[226],[227], chicken fat [228], catfish oil [207], *Helianthus annuus* L oil [229], cotton oil [230] and sativa oil [231] for FAME production. In 2014, Niju *et al.* [209] examined a highly active modified chicken eggshell derived CaO catalyst for the synthesis of FAME from WFO. The authors reported that highly reactive CaO can be obtained from eggshells *via* calcination-hydration-dehydration treatment. While the FAME conversion was only 67.57 % for commercial CaO catalyst, CaO obtained from the eggshell calcined at 900 °C followed by hydration and dehydration at 600 °C (Eggshell-CaO-900-600) gave 94.52 % conversion under the optimized reaction conditions. Calcination followed by hydration and dehydration greatly increased the surface area of the eggshell derived CaO as compared to those obtained with the only calcination. The high activity of the modified CaO (Eggshell-CaO-900-600) is attributed to the high surface area (8.6401 m^2g^{-1}) compared to both commercial CaO (3.0022 m^2g^{-1}) and eggshell derived-CaO calcined at 900 °C (eggshell-CaO-900) (3.7262 m^2g^{-1}). The basicity of modified catalyst lies in the region $12.2<H\_<15.0$. Figure 25b depicted the SEM image of CaO generated from the calcination–hydration–dehydration treatment of eggshells (i.e. egg shell-CaO-900-600) which shows a honeycomb-like porous surface. However, in the case of the eggshell-CaO-900, rod-like structure with microporous particles (size ranging from 1.29 to 2.0 μm) was observed (Figure 25a).

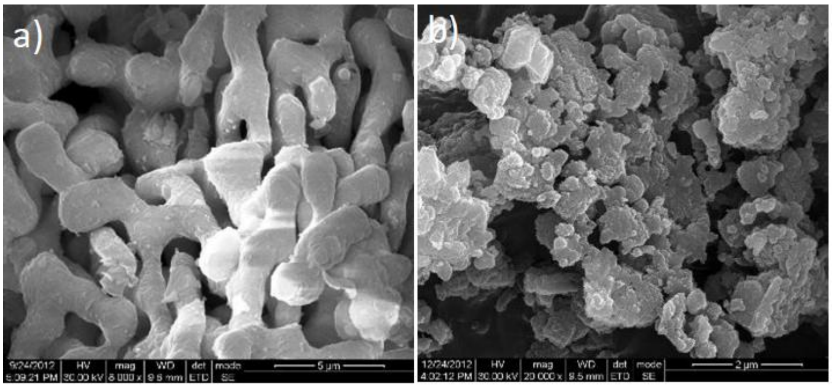


Figure 25: SEM image of a) eggshell-CaO-900. b). Eggshell-CaO-900-600. Adapted from ref. [209].

In another work, waste chicken fat obtained from slaughterhouse was converted to FAME using calcined chicken eggshell catalyst under microwave irradiation (Figure 26) [228]. Esterification was carried out to lessen FFA content of the chicken oil below 1 mg KOH/g of oil, followed by transesterification to yield FAME. Flow diagram of biodiesel production using chicken eggshell as a catalyst is presented in Figure 27. Optimization of transesterification process parameters by response surface methodology was performed.

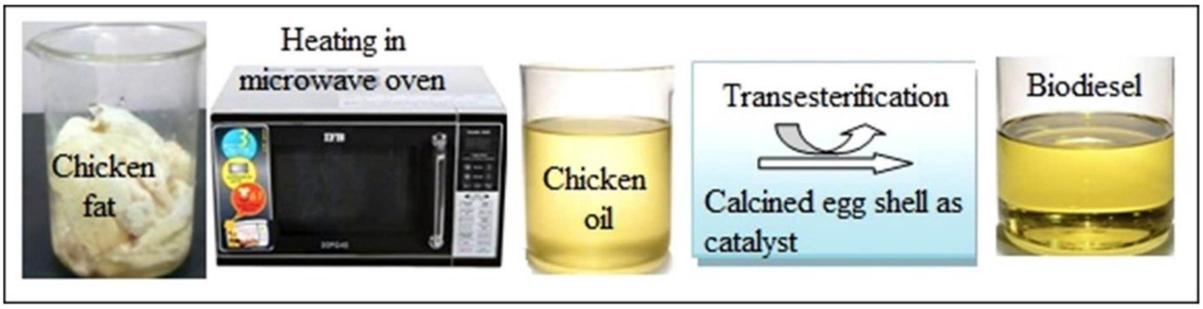


Figure 26: Microwave-assisted synthesis of FAME using an eggshell catalyst. Adapted from ref. [228].

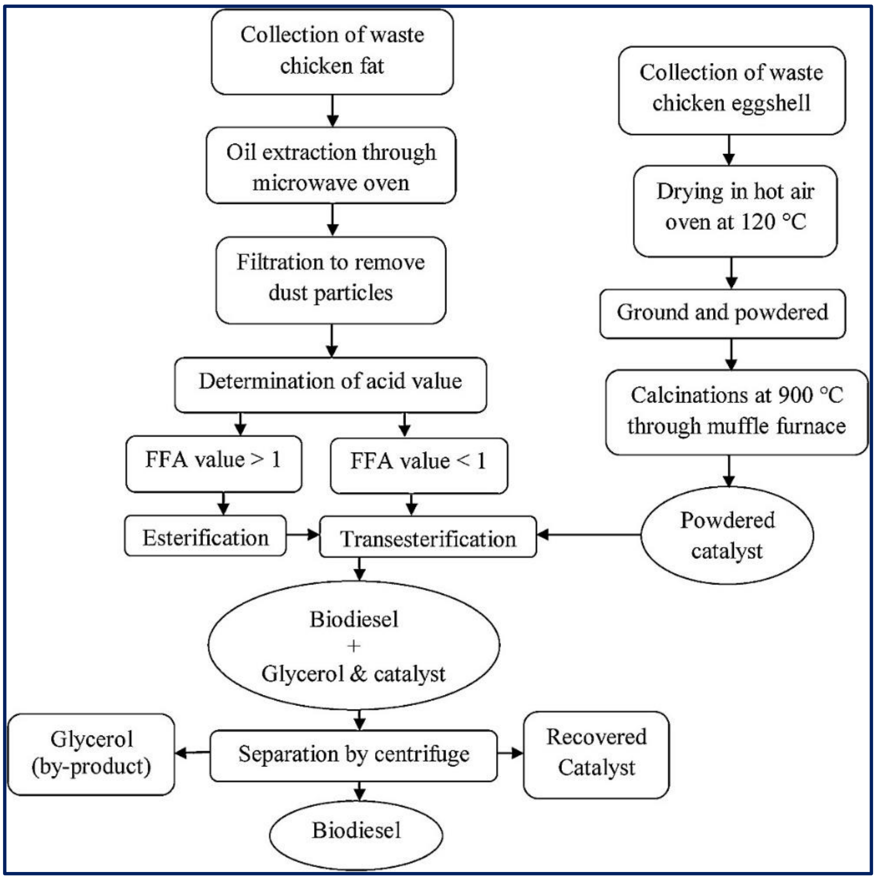


Figure 27: Flow diagram of biodiesel production utilizing chicken eggshell catalyst. Adapted from ref. [228].

Similarly, *Helianthus annuus* L oil was converted to FAME using eggshell derived CaO [229]. The preparation route of CaO starting from the shell is presented in Figure 28. Under the optimized reaction conditions, 99.2 % of FAME yield was achieved. The catalyst is stable up to the fourth cycle where 87.8 % yield was observed.

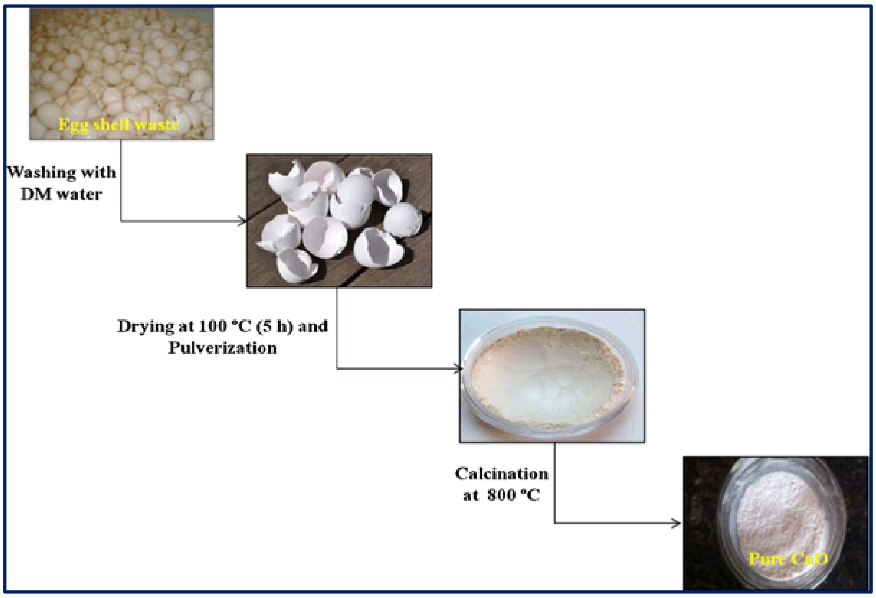


Figure 28: Schematic layout for eggshell originated CaO synthesis. Adapted from ref. [229]

Earlier, Ansori *et al.* [232] reported a chicken shell derived CaO catalyzed synthesis of FAME from *C. inophyllum* L oil under a microwave (MW) irradiation. Initially, oil FFA content was pre-esterified utilizing H_2SO_4, which was then transesterified by utilizing the CaO catalyst (originated from chicken shell) and reported 98.90 % FAME yield in 12.47 min. In another work, Mansir *et al.* [233] examined the application of W/Mo/CaO catalyst, where tungsten and molybdenum were impregnated on CaO derived from waste eggshell, for the transformation of WCO *via* concerted esterification/transesterification to produce FAME in a one-pot process. Moreover, the authors investigated the influence of W and Mo loading on CaO in its catalytic activity and found that catalytic activity increased when wt. % of W is higher than wt. % of Mo over the range of 0.3-0.7 %. A maximum yield of 96.2 % was reported under the optimum reaction conditions using 0.6 W/0.4 Mo/CaO. In addition, several literatures are available for the transesterification of WCO having FFA content in the range of 4-7.1 % to produce methyl ester using various eggshell derived CaO catalyst impregnated with acidic and basic compounds. Examples of such catalysts are CaO/anthill [234], CaO/Zn [235], $CaO/KF/Fe_3O_4$ [236], CaO/SiO_2 based on palm empty fruit bunch (PEFB) [237], and Mo-Zr/CaO [238] etc.

In 2015, Joshi *et al.* [239] synthesized various metal oxides, for example, ZnO, MnO_2, Fe_2O_3 and Al_2O_3 impregnated on CaO derived from eggshell via calcination at 900 °C and exploited these catalysts in the conversion of non-edible JCO to FAME. Among all the mixed metal oxides, the surface area and pore volume of ZnO-CaO is highest and thus showed an excellent 95.2 % JCO conversion. The authors also reported that the catalyst is very stable towards the transesterification of JCO and can be reused for 4 cycles. Similarly, Teo *et al.* [240] synthesized CaO NPs derived from *Gallus domesticus* eggshell *via* precipitation method and utilized it for the conversion of JCO to give FAME with 97 % yield under the optimal reaction conditions. TEM images and particle size distribution of waste eggshell of *Gallus domesticus* derived nano-CaO catalyst is displayed in Figure 29 which revealed that the particles were regular spheroidal shape and the average particle diameter is 16-27 nm. Figure 30 displays the basicity measurement of the catalyst and commercial CaO using CO_2-TPD technique. All CaO catalysts showed a broad desorption peak owing to the existence of strong basic strength. The desorption peaks of both catalysts observed over the temperature ranging from 550 to 700 °C are attributed to the super-basic characteristics of the nanoparticles.

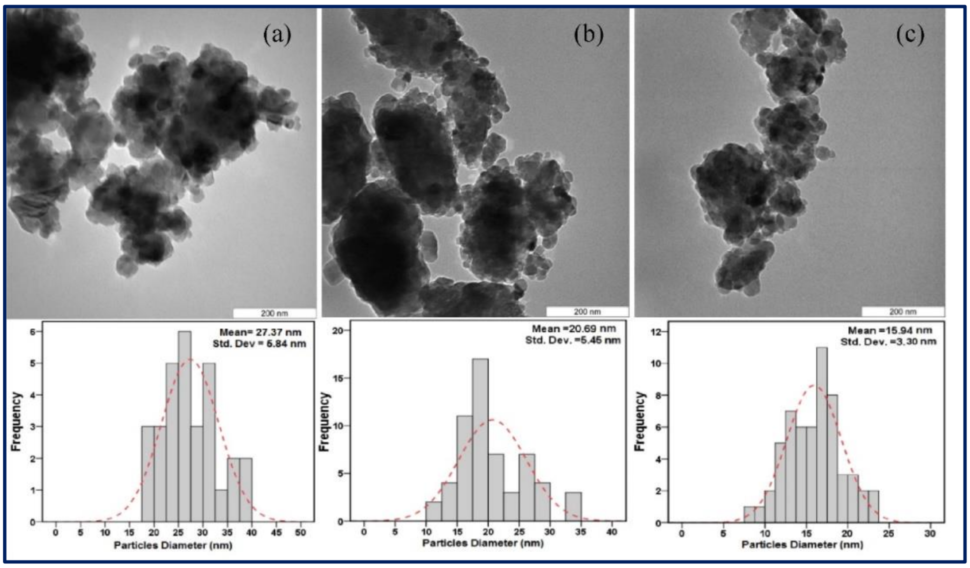


Figure 29: TEM images and particle size distributions of surfactant assistant CaO nanocatalysts: after 40 min (a); after 80 min (b) and after 120 min (c). Adapted from ref. [240].

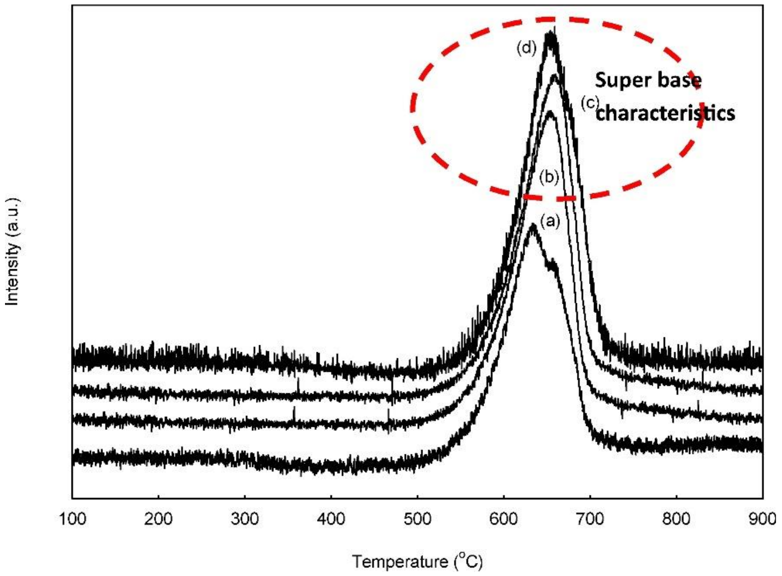


Figure 30: CO_2 desorption performance commercial of CaO (a) and nano CaO catalysts: after 40 min (b); after 80 min (c) and after 120 min (d). Adapted from ref. [240]

In 2011, Olutoye *et al.* [241] reported a mixed metal solid catalyst, where $Mg(NO_3)_2$ and KNO_3 were impregnated on CaO originated from eggshell and exploited it in the transformation of palm oil to FAME. The authors made three sets of a catalyst by changing the loading amount of $Mg(NO_3)_2$ and KNO_3 on CaO with wt. % ratio of 6:1:1, 2:1:1 and 1:1.5:1.5 and investigated their influence on the transesterification reaction and reported that the catalyst with wt. % ratio of 6:1:1 showed the maximum yield of 85.8 %. In addition, several works are reported in the literature regarding the transesterification of palm oil using chicken shell derived CaO modified solid catalyst such as CaO/SiO_2 [242],[243] CaO/rice husk [244] etc. Recently, Sulaiman *et al.* [245] successfully synthesized a mixture of calcined coconut waste and egg waste for the transformation of palm oil to biodiesel. The authors employed RSM based on CCD to study the ideal reaction conditions: coconut waste/eggshell waste ratio, M/O molar ratio, catalyst amount, reaction temperature and reaction time. After a successful investigation, they reported that 5:1 wt. % ratio of coconut waste/eggshell waste showed the maximum yield of 81 % under the optimal reaction conditions.

In another work, A Li doped CaO catalyst derived from eggshell was examined for the transformation of nahor oil to produce FAME by Boro *et al.* [246]. They measured the FFA content in the nahor oil and found 15 mg KOH/g. Due to this high FFA contents, a two-step process was investigated; firstly, esterification was performed using sulfuric acid to bring down FFA amount up to <1 followed by transesterification reaction using Li/CaO catalyst. They also examined the impact of Li doping on the conversion of oil to FAME and reported a maximum 94 % conversion when the Li doping was 2 wt. %. Recently, Rahman *et al.* [247] modified CaO derived from chicken eggshell with transition metals such as Zn and Cu and applied the catalyst in the transformation of eucalyptus oil to FAME. The authors reported that the surface area and basicity of Zn/CaO are higher than the Cu/CaO, therefore Zn/CaO showed better result with 93.2 % FAME yield. Moreover, the impregnation of Zn on CaO improved the stability of the catalyst and can be used for 7 consecutive cycles. In another report, a magnetically recoverable KF modified CaO derived from eggshell was prepared and employed in the transformation of neem oil to FAME [236]. The author reported that the primary advantage of the catalyst is that the catalyst circumvented saponification reaction and therefore transesterification of neem oil (FFA content 4.2 %) can proceed through the one-step process, and 94.5 % FAME can be achieved.

In 2010, a novel eggshell originated CaO impregnate on fly ash was reported for the transesterification of soybean oil to form FAME. The influence of CaO loading was studied by the authors and found that 30 wt. % CaO loading showed a maximum yield of 96.97 %. Moreover, CaO supported on fly ash enhanced catalyst reusability and reactivity compared to neat eggshell originated CaO [248]. In addition, a KF modified CaO originated from eggshell was examined for the transformation of soybean oil to FAME. The modified catalyst has higher basicity than the neat CaO due to the addition of KOH in the process [249]. Recently, Chowdhury *et al.* [250] synthesized a Na-doped CaO derived from chicken eggshell and exploited it in the transesterification of *Madhuca indica* oil. A two-step process was employed as the oil have 45 % of FFA content. They first esterified the oil using 5 wt. % sulfuric acid to lessen FFA content of the oil followed by transesterification using Na-doped CaO catalyst. To study the influence of reaction parameters on the transformation of oil to biodiesel, Taguchi approach was used, where they observed that M/O molar ratio and the reaction temperature have the highest impact and reaction time has the minimal impact on the transformation of oil to FAME. In 2014, Chen *et al.* [251] demonstrated the synthesis of FAME from palm oil using CaO catalyst derived from ostrich egg-shell *via* ultrasonication. They compared the production of biodiesel using both mechanical stirring and ultrasonication process and reported that the latter case showed higher yield (92.7 %). Moreover, the catalyst can be used for 8 consecutive cycles. A transesterification process for soybean oil deodorizer distillate (SODD) to produce FAME was reported using CaO derived from the duck eggshell. They measured the FFA content of SODD and found 53.2 %, therefore to overcome the saponification problem the oil was pre-esterified with sulfuric acid and then the transesterification was performed of the pre-esterified SODD oil using CaO catalyst to produce FAME with an overall yield of 94.6 % [2]. In addition, CaO derived from quail eggshell were also utilized for the transformation of palm oil [252] and JCO [253] to biodiesel in high yield.

Table 15: Various eggshells derived solid base catalyst for FAME production.

No.	Catalyst source	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	Chicken eggshell	CaO	Soybean oil	9:1, 3, 65, 180	>95	[198]
2.	Chicken eggshell	CaO	Soybean oil	10:1, 7, 57.5, 120	93	[199]
3.	Chicken eggshell	CaO	Soybean oil	8:1, 10, 65, 180	90	[200]
4.	Chicken eggshell	CaO	Soybean oil	14:1, 4, 60, 180	91	[201]
5.	Ostrich eggshell	CaO	Karanja oil	8:1, 2.5, 65, 150	95	[202]
6.	Chicken eggshell	CaO	WCO	22.5:1, 3.5, 65, 330	91	[203]
7.	Chicken eggshell	CaO	WCO	12:1, 1.5, 65, 120	94	[204]
8.	Chicken eggshell	CaO	WCO	4:1, 2, 65, 120	NR	[205]
9.	Chicken eggshell	CaO	WFO	9:1, 3, 65, 180	95.05	[206]
10.	Chicken eggshell	CaO	WCO	12:1, 1.5, 60, 60	96.23	[207]
11.	Chicken eggshell	CaO	WCO	24:1, 4, 60, 240	100	[208]
12.	Chicken eggshell	CaO	WCO	12:1, 5, 65, 60	94.52^{b}	[209]
13.	Chicken eggshell	CaO	WCO	10:1, 1.5, 60, 50	96.07	[210]
14.	Chicken eggshell	CaO	WCO	6:1, 3, 60, 30	97.50	[211]
15.	Chicken eggshell	CaO	WCO	9:1, 5, 65, 165	87.8	[212]
16.	Chicken eggshell	CaO	WCO	15:1, 6, 65, 420	75.92	[213]
17.	Chicken eggshell	CaO	Palm oil	18:1, 10, 60, 90	>90	[214]
18.	Chicken eggshell	CaO	Palm oil	18:1, 15, 900 W, 4	96.7	[215]
19.	Chicken eggshell	CaO	Palm oil	12:1, 10, 60, 120	94.1	[216]
20.	Chicken eggshell	CaO	Palm oil	6:1, 5, NR, 30	95	[217]
21.	Chicken eggshell	CaO	Rape seed oil	9:1, 3, 60, 180	96	[218]
22.	Chicken eggshell	CaO	Rapeseed oil	9:1, 4, 60, 60	95.12	[219]
23.	Chicken eggshell	CaO	Sunflower oil	9:1, 3, 60, 180	96	[220]

24.	Chicken eggshell	CaO	Sunflower oil	11:1, 5, 60, 3	83.2	[221]
25.	Chicken eggshell	CaO	Sunflower oil	9:1, 3, 60, 240	97.75	[222]
26.	Chicken eggshell	CaO	Sunflower oil	12:1, 2, 60, 180	100	[223]
27.	Chicken eggshell	CaO	JCO	81, 2, 65, 150	90	[224]
28.	Chicken eggshell	CaO	Microalgae *Chlorella vulgaris*	10:1, 1.39, 70, 180	92.03	[225]
29.	Chicken eggshell	CaO	Microalgae	10:1, 1.7, 70, 216	86.41	[226]
30.	Chicken eggshell	CaO	Micro algae/ *S. armatus*	10:1, 1.61, 75, 240	90.44	[227]
31.	Chicken eggshell	CaO	Chicken fat	13:1, 8.5, 57.5, 300	90.41	[228]
32.	Chicken eggshell	CaO	Catfish oil	12:1, 1.5, 60, 60	87.77	[207]
33.	Chicken eggshell	CaO	*Helianthus annuus* L oil	8:1, 2.5, 65, 120	99.2	[229]
34.	Chicken eggshell	CaO	Cotton oil	9:1, 3, 60, 180	98.08	[230]
35.	Chicken eggshell	CaO	*C. sativa* oil	12:1, 1, 65, 120	97.2	[231]
36.	Chicken eggshell	CaO	*C. inophyllum* L oil	9:1, 3.88, MW, 12.47	98.90	[232]
37.	Chicken eggshell	CaO/W/Mo	WCO	15:1, 2, 70, 120	96.2	[233]
38.	Chicken eggshell	CaO/anthill	WCO	6:1, 5, 60, 120	70	[234]
39.	Chicken eggshell	CaO/Zn	WCO	20:1, 5, 65, 240	96.74	[235]
40.	Chicken eggshell	CaO/KF/Fe_3O_4	WCO	15:1, 6, 65, 120	97	[236]
41.	Chicken eggshell	CaO/SiO_2 based on PEFB	WCO	14:1, 8, 60, 90	96	[237]
42.	Chicken eggshell	Mo-Zr/CaO	WCPO	15:1, 3, 80, 180	90.1	[238]
43.	Chicken eggshell	ZnO/CaO	JCO	12:1, 5, 65, 60	98.2	[239]
44.	Chicken eggshell	CaO NPs	JCO	6:1, 2, 90, 120	98	[240]

45.	Chicken eggshell	$K_y(MgCa)_{2x}O_3$	Palm oil	16:1, 5.53, 65, 273	88	[241]
46.	Chicken eggshell	CaO/SiO_2	Palm oil	15:1, 9, 65, 480	80.21	[242]
47.	Chicken eggshell	CaO/SiO_2	Palm oil	15:1, 3, 60, 120	87.5	[243]
48.	Chicken eggshell	CaO/Rice husk	Palm oil	9:1, 7, 65, 240	91.5	[244]
49.	Chicken eggshell	CaO/Coconut waste	Palm oil	24:1, 5, 65, 180	81	[245]
50.	Chicken eggshell	Li/CaO	Nahor oil	10:1, 5, 65, 240	94	[246]
51.	Chicken eggshell	CaO/Zn	Eucalyptus oil	6:1, 5, 65, 150	93.2	[247]
52.	Chicken eggshell	$CaO/KF/Fe_3O_4$	Neem oil	15:1, 6, 65, 120	97	[236]
53.	Chicken eggshell	CaO/fly ash	Soybean oil	6.9:1, 1, 70, 300	96.97	[248]
54.	Chicken eggshell	CaO/KF	Soybean oil	12:1, 2, 65, 120	99.1	[249]
55.	Chicken eggshell	Na/CaO	*Madhuca indica* oil	9:1, 5, 60, 120	81.1	[250]
56.	Ostrich eggshell	CaO	Palm oil	9:1, 8, 60, 60	92.7	[251]
57.	Duck eggshell	CaO	SODD	10:1, 10, 60, 80	94.6	[2]
58.	Quail eggshell	CaO	Palm oil	12:1, 1.5, 65, 120	98	[252]
59.	Quail eggshell/ crab shell	CaO	Jatropha oil	18:1, 4, MW, 5	94	[253]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

^{b}Conversion

NR= Not reported

WCPO= Waste cooking palm oil

8.1.7.2.2. Mollusk shell and other seashells

Mollusk shell and other seashells derived solid catalyst has been widely investigated in the transformation of edible/non-edible oils to produce biodiesel, and are listed in Table 16. Examples are a basic solid catalyst developed by impregnation of KI on the calcined oyster shell which was utilized in the transformation of soybean oil to FAME. The authors reported that impregnation and calcination increase the surface area to an extent of 32 fold and therefore increases the catalytic activity. The main disadvantages of the catalyst are the reusability factor and higher loading of KI [254]. In addition, there is various literature where neat CaO derived from oyster shell were utilized for transformation of soybean oil to FAME [255] and microwave-assisted (800 W) biodiesel synthesis from jatropha oil [256]. Recently, a basic heterogeneous catalyst was developed from the river snail shell by calcination at 800 °C for 4 h. The catalyst was employed for the transesterification of WCO for biodiesel production. They performed KOH titration and found that FFA content in the WCO is 0.3 %, therefore direct transesterification was carried out and 98.19 % yield was achieved under the optimal reaction conditions [257]. Elsewhere other reports are also available where CaO derived from calcined river snail were used for the transesterification of various edible/non-edible oils, for example, palm oil [258], soybean oil [259] and WFO [260].

In 2016, Liu *et al.* developed a solid catalyst, where KBr was loaded on calcined snail shell and kaoline mixture followed by activation of the catalyst *via* calcination at 500 °C for 4 h and applied the catalyst in the transformation of soybean oil to FAME. They also investigated the effect of loading of KBr and wt. % ratio of snail shell/kaoline mixture on biodiesel yield and found that the catalyst showed a maximum yield of 98.5 % when the KBr loading and wt. % ratio of snail shell/kaoline were 40 wt. % and 4:1, respectively. Mixing of snail shell and kaoline together provides the catalyst extra stability compared to their pure form [261]. In addition, Laskar *et al.* [262] developed a solid basic catalyst CaO derived from a calcined snail shell for the conversion of soybean oil to biodiesel. Under the ideal reaction states, 98 % biodiesel yield was achieved. It is reported that at 400-600 °C calcination temperature, $CaCO_3$ of snail shell transformed to calcite. When calcination temperature was further increased to 700 and 800 °C, a minor and major component of CaO was achieved, which was later completely transformed into CaO at 900 °C calcination temperature. Figure 31 reveals that 100 % transformation of $CaCO_3$ into CaO can be achieved above 800 °C calcination temperature.

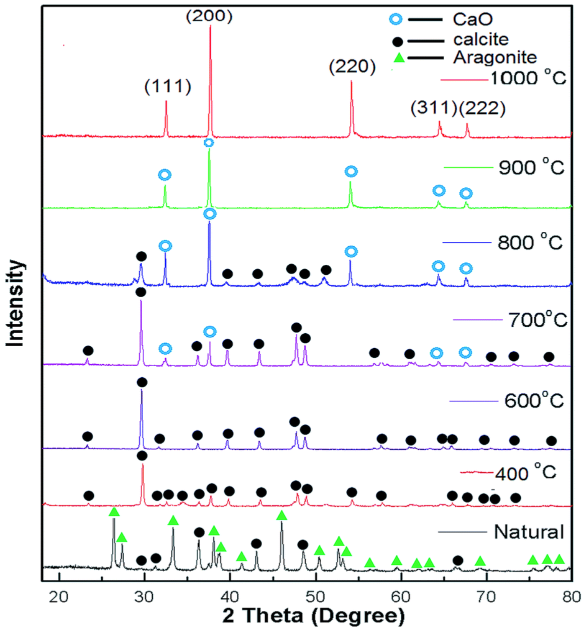


Figure 31: XRD spectra of normal and calcined (400-1000 °C) snail shells. Adapted from ref. [262].

In another work, El-Gendy *et al.* [263] reported CaO catalyst originated from snail shell calcined at 800 °C and utilized it in the transesterification reaction. RSM was utilized to investigate the influence of reaction parameters on the biodiesel production and reported that 96.76 % yield was observed under the optimized reaction conditions. Similarly, various literature is available for the transesterification of WCO to FAME using CaO derived from snail shell collected from different sources [264],[265]. Very recently, Krishnamurthy *et al.* [266] developed a solid catalyst, CaO nanoparticles derived from snail shell *via* the hydrothermal method and investigated its application in the transesterification of *H. wightiana* oil to produce FAME. However, a high FFA content (7.57 %) in the oil led the authors to follow a two-steps process: 1) pre-esterification and 2) transesterification for the production of FAME. RSM was utilized to examine the impact of reaction parameters on FAME synthesis, reported 96.92 % yield under the optimal reaction conditions. In a similar vein, CaO derived from snail shell was also investigated for the transformation of *A. africana* seed oil [267] and showed 85 % FAME yield.

A calcined mussel/cockle/scallop shell derived CaO was developed for the transformation of palm oil for FAME production. The authors reported high catalyst reactivity catalytic activity with great stability towards the transesterification of palm oil with 95 % conversion [268]. In the meantime, Hadiyanto *et al.* [269] developed a solid catalyst, modified

CaO (derived from green mussel shell) with activated carbon (C) followed by impregnation on NaOH and utilized the catalyst in the transformation of palm oil. The wt. % C/CaO ratio of 2:3 showed the maximum yield of 95.12 % under the optimal reaction conditions. Similarly, KOH impregnated mussel shell derived CaO was examined for castor oil transformation to biodiesel. The authors made a comparison between non-impregnated and KOH impregnated catalysts and revealed that the KOH impregnated catalyst displayed higher reactivity as well as basicity and reported 91.7 % FAME yield using KOH impregnated catalyst [270]. Moreover, calcined mussel shell derived catalyst were widely examined for the transformation of vegetable oils, for example, soybean oil [271,272] Chinese tallow oil [273], *Camelina sativa* oil [274] etc., for biodiesel production.

Syazwani *et al.* [275] examined CaO, originated from angel wing shell (AWS) calcined at 900 °C for 2 h, for the conversion of *N. oculata* micro-algae oil to FAME. The catalyst possessed high reactivity with great stability and can be reused for 3 consecutive cycles. Furthermore, a bifunctional catalyst was developed for conversion of palm fatty acid distillate (PFAD) to FAME. The angel wing shell was calcined to form CaO followed by sulfonation to afford the catalyst. The authors reported that the catalyst surface area increased to two-fold after the modification, as a result, the catalyst showed excellent activity towards the esterification of PFAD. Unfortunately, the catalyst was reusable only for two cycles as blocking of active sites occurred in each reaction cycles. Therefore to enhance the reusability of the catalyst, pretreatment of the catalyst such as washing and re-calcination are necessary before each reaction cycles [276]. In 2015, Asikin-Mijan *et al.* [277] developed a waste clam shell derived CaO using hydration-dehydration treatment and investigated its catalytic application in the conversion of palm oil to FAME. They also examined the effect of hydration-dehydration time on biodiesel conversion and found that higher is the hydration time higher is the catalytic activity as hydration for longer-term enhanced the formation of $Ca(OH)_2$ and thus increased the basicity, reduced the crystallinity and also enhanced the surface area. They reported that the rehydration for 12 h showed the maximum 98 % FAME yield under optimized reaction conditions. Similarly, investigation of naked CaO catalyst, derived from a calcined short-necked clamshell, recorded 93 % biodiesel yield under the optimal reaction conditions [278]. In addition, CaO derived from various calcined clamshell were utilized for the transformation of diverse edible/non-edible oils, for example, palm oil [279],[280], WFO [281] etc., to produce biodiesel.

A solid ethanol-treated catalyst CaO, derived from calcined abalone shell was examined for production of FAME from palm oil. The authors investigated the impact of ethanol treatment at different temperature (RT, 100 °C and 160 °C) and found that the catalyst treated with ethanol at 100 °C showed the maximum yield of 96.2 % as ethanol treatment provides high basicity, high surface area and lowered the catalyst crystallinity. Moreover, comparison of modified CaO with naked CaO showed that modified CaO has higher reusability and provided higher biodiesel yield [282]. In addition, there are several reports available in literature regarding the transesterification of palm oil to FAME utilizing CaO based solid catalyst originated from various waste shells such as *T. jourdani* shell [283], *A. cristatum* shell [284], cockle shell [285] and obtuse horn shell [286] etc.

In 2009, Xie *et al.* [287] synthesized a solid catalyst via three-step: i) incomplete carbonization of a biont shell at 500 °C, ii) KF impregnation and iii) catalyst activation at 300 °C. The developed catalyst was utilized for conversion of rapeseed oil to FAME. They reported that the catalyst displayed excellent reactivity due to the formation of a higher amount of active sites during the reaction between incomplete carbonized shell and KF. The effect of KF loading was also examined and found that 25 % KF loading is optimal and showed 97 % FAME yield under the optimized reaction conditions. Correspondingly, Boro *et al.* [288] demonstrated the synthesis of CaO catalyst by calcination of *Turbonilla striatula* shell and utilized it for transformation of mustard oil to FAME. The effect of calcination temperature was examined and observed that the catalyst calcined at 900 °C displayed maximum 93.3 % FAME yield. In addition, CaO derived from calcined *Turbonilla striatula* was modified with Ba in the range of 0.5-1.5 wt. % and utilized it for the transformation of WCO to biodiesel. Due to the high acid value 22 mg KOH/g, the oil was pretreated with sulfuric acid to reduce the acid value <1. Then the pretreated oil was transesterified with Ba/CaO catalyst. The authors also examined the effect of Ba loading and found that 1 % of Ba doped showed >98 % biodiesel yield [289]. In addition, *Chicoreus brunneus* shell was calcined above 800 °C to convert $CaCO_3$ to CaO followed by hydration/dehydration to form a solid base catalyst and examined it for the transformation of rice bran oil. Calcination and hydration provide the catalyst high porosity, enhances the basicity, catalytic activity and reusability [290]. In addition, shrimp shell originated catalysts has also been utilized for transformation of various edible/non-edible oils to FAME. Yang *et al.* [291] synthesized a catalyst *via* a three steps processes; (i) inadequate carbonization of shrimp shell, (ii) reaction with KF and (iii) activation of the catalyst under the heating condition for the rapeseed oil transformation. The authors examined the impact of carbonization temperature, KF amount and activation temperature and found that 89.1 % biodiesel was achieved under the reaction states: carbonization temperature of 450 °C, KF amount of 25 wt. % and an activation temperature of 250 °C. The excellent catalyst reactivity is attributable to the formation of active sites during the reaction between incomplete carbonized shrimp shell and KF. Moreover, a solid catalyst, CaO nanoparticles with a diameter of 66 nm derived from *Polymedosa erosa* shell *via* calcination-hydration-dehydration process was developed for the transformation of JCO to FAME in a two-step procedure: 1) pre-esterification and 2) transesterification. The influence of reaction parameters on the oil conversion was examined by RSM technique and displayed 98.54 % FAME yield [292].

In the recent past, Sivakumar *et al.* [293] developed a solid catalyst derived from *Scylla Tranquebarica* crab shell calcined at 750 °C for sunflower oil transformation to FAME. The developed catalyst displayed similar reactivity to that of commercial CaO and reported a very high conversion of 94.2 % under the optimal reaction conditions. Similarly, Shankar *et al.* [294] prepared a solid catalyst where CaO (derived from crab shell calcined at 900 °C) impregnated on Na-ZSM-5 followed by activation at 550 °C for 10 h and utilized it for production of FAME from neem oil. The impact of CaO loading was examined and found that 15 wt. % CaO impregnation showed a maximum 95 % biodiesel formation. Moreover, various reports are available for the transesterification of edible/non-edible oils such as palm oil [295] and karanja oil [296] utilizing CaO originated from calcined crab shells.

Table 16: Various mollusk and seashells derived solid catalyst for biodiesel production.

No.	Catalyst source	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	Oyster shell	CaO/KI	Soybean	10:1, 1mmol/g, 50, 240	79.5	[254]
2.	Oyster shell	CaO	Soybean oil	6:1, 25, 65, 300	73.8	[255]
3.	Oyster and *Pyramidella* shells	CaO	Jatropha oil	15:1, 4, MW, 6	93	[256]
4.	River snail shell	CaO	WCO	9:1, 3, 65, 60	92.5^b	[257]
5.	River snail shell	CaO	Palm oil	12:1, 5, 65, 90	98.5	[258]
6.	River snail shell	CaO	Soybean oil	9:1, 3^c, 65, 180	98	[259]
7.	River snail shell	CaO	WFO	6.03:1, 2, 60, 420	87.28	[260]
8.	Snail shell	CaO/KBr/kaolin	Soybean oil	6:1, 2, 65, 120	98.5	[261]

9.	Snail shell	CaO	Soybean oil	6:1, 3, RT, 420	98	[262]
10.	Snail shell	CaO	WFO	6:1, 3, 60, 60	96	[263]
11.	Snail shell	CaO	WCO	9:1, 9, 60, 180	84.14	[264]
12.	Snail shell (*S. canarium*)	CaO	WCO	12:1, 3, 65, 240	83.5	[265]
13.	Snail shell	Nano-CaO	*H. wightiana* oil	12.4:1, 0.892, 61.6, 145.154	98.93	[266]
14.	Snail shell	CaO	*A. africana* seed oil	6:1, 1.5, 55, 65	85	[267]
15.	Mussel/cockle/scallop shell	CaO	Palm oil	9:1, 10, 65, 180	95	[268]
16.	Mussel shell (*Perna varidis*)	C/CaO/NaOH	Palm oil	0.5:1, 7.5, 65, 180	95.12	[269]
17.	Mussel shell	CaO/KOH	Castor oil	6:1, 2, 60, 180	91.17	[270]
18.	Mussel shell	CaO	Soybean oil	24:1, 12, 60, 480	94.1	[271]
19.	Mussel shell	CaO	Soybean oil	9:1, 4, 65, 180	>98[b]	[272]
20.	Fresh water mussel shell	CaO	Chinese tallow oil	12:1, 5, 70, 90	97.5	[273]
21.	Mussel/clamp/oyster	CaO	*Camelina sativa* oil	12:1, 1, 65, 120	95/93/91	[274]
22.	Angel wing shell	CaO	*N. oculata* (Microalgae) oil	150:1, 9, 65, 60	84.11	[275]
23.	Angel wing shell	$CaO\text{-}SO_4$	PFAD	15:1, 5, 80, 180	98[b]	[276]
24.	Clamshell	CaO	Palm oil	9:1, 1, 65, 120	98	[277]
25.	Short necked clam (*O. orbiculata*) shell	CaO	JCO	20:1, 4, 65, 360	93	[278]
26.	Clamshell (*M. mereterix*)	CaO	WFO	6.03:1, 3, 60, 180	> 89	[279]
27.	White bivalve clamshell	CaO	WFO	18:1, 8, 65, 180	95.84	[280]

28.	Venus clam (*Tapes belcheri S.*)	CaO	Palm oil	15:1, 5, 65, 360	97	[281]
29.	Abalon shell	CaO	Palm oil	9:1, 7, 65, 150	96.2	[282]
30.	*T. jourdani* shell	CaO	Palm oil	3:1, 10, 80, 420	99.33[b]	[283]
31.	*A. cristatum* shell	CaO	Palm oil	8:1, 3, 60, 360	93	[284]
32.	Cockleshell	CaO	Palm oil	0.54:1, 4.9, reflux, 180	99.4	[285]
33.	Obtuse horn shell	CaO	Palm oil	12:1, 5, reflux, 360	86.75	[286]
34.	Biont (turtle) shell	CaO/KF	Rape seed oil	9:1, 3, 70, 180	97.5	[287]
35.	*Turbonilla striatula* shell	CaO	Mustard oil	9:1, 3, 65 ±5, 360	93.3	[288]
36.	*Turbonilla striatula* shell	CaO/Ba	WCO	6:1, 1, 65, 120	> 98[b]	[289]
37.	*Chicoreus brunneus* shell	CaO	Rice bran oil	30:1, 0.4, 65, 120	93	[290]
38.	Shrimp shell	CaO/KF	Rape seed oil	9:1, 2.5, 65, 180	89.1[b]	[291]
39.	*P. erosa* seashells	Nano-CaO	Jatropha oil	5.15:1, 0.02, RT, 133.1	95.8	[292]
40.	Crab shell (*S. tranquebarica*)	CaO	Sunflower oil	12:1, 8, 95, 75	94.2	[293]
41.	Crab shell	CaO/Na-ZSM-5	Neem oil	12:1, 15, 75, 360	95	[294]
42.	Crab shell (*S. serrata*)	CaO	Palm oil	0.5:1, 5, 65, 150	98.8	[295]
43.	Crab shell	CaO	Karanja oil	8:1, 2.5, 65, 120	94	[296]

[a] Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).

[b] Conversion

[c] w/w

PFAD = palm fatty acid distillate

8.2 Acid catalysts

Acid can catalyze both transesterification and esterification reactions without soap formation [297]. Hence, unlike base catalysts, an acid catalyst has the potential to afford biodiesel from poor quality oil with high FFA and high water content. In the transesterification reaction, alkaline catalysts are superior in promoting methoxide anion formation from methanol. In contrary to it, acidic catalysts are less active in methoxide anion formation, but could activate the carbonyl bonds via H^+ addition (Brønsted acidic sites) or via coordination of the carbonyl oxygen with the coordinatively unsaturated metal ion sites (Lewis acidic sites), and thereby promote transesterification. Hence, an increase in the number of either Brønsted or Lewis acidic sites promotes faster FAME formation *via* transesterification. Delightfully, heterogeneous acid catalysts are endorsed as a potential alternative to homogenous acids catalysts as it possesses certain advantages like it can be easily separated and reused, less corrosive and less toxic [298]. In recent years, several research groups have studied the feasibility of solid acid catalysts for esterification/transesterification processes and proposed economical and environment-friendly approaches for biodiesel production [299],[300],[301].

8.2.1 Mixed metal oxides

A wide range of mixed metal oxide acid catalysts has been utilized to overcome the problem associated with high FFA content in low-cost biodiesel feedstock employed in FAME production (Table 17). Suzuta *et al.* [302] reported utilization of Fe_2O_3-SiO_2 catalyst in the conversion of JCO to FAME. The catalyzed reaction displayed 95.6 % FAME yield under the optimized reaction conditions. When Fe loading was raised from 0.07 to 2.1 wt. %, the acidity of the catalyst increased drastically. Fe-oxide species scattered over the SiO_2 surface were recognized as the active sites. In the meantime, $ZnAl_2O_4$/$ZnFe_2O_4$ catalyst was also examined for the transformation of oil such as sunflower oil, WCO and JCO [303]. During the reaction, the Zn 3d electrons of $ZnAl_2O_4$ and $ZnFe_2O_4$ spinels were likely to take part in the electronic excitation, thereby Zn 3d electrons are probably going to undertake a vital job to enhance the catalyst reactivity. In 2012, Xie *et al.* [304] synthesized SnO_2-SiO_2 catalyst by loading 8 wt. % Sn onto SiO_2 followed by calcination (550 °C) and exploited it in the transformation of soybean to FAME yielding 81.7 % under the optimal reaction conditions of M/O molar ratio of 24:1, catalyst loading of 5 wt. %, reaction temperature of 180 °C within 5 h.

Impregnation followed by calcination (600 °C) was used to synthesize Fe-Mn-MoO_3/ZrO_2 catalyst, which could provide a high 95.6 ± 0.15 % yield of FAME [305]. It is interesting to observe that ZrO_2 and MoO_3/ZrO_2 gave a lower FAME yield of 48.6 ± 1.14 and

73.0 ± 0.25 % respectively. The high activity of Fe-Mn-MoO_3/ZrO_2 catalyst is attributed to high surface area (49.5 m^2g^{-1}) and availability of huge active sites (2411 $\mu molg^{-1}$) in the catalyst. Moreover, catalyst reusability examination revealed that it is stable up to 6 progressive reaction cycles of transesterification of WCO without loss in its efficiency. On the other hand, enhanced catalytic activity was observed in a mixed metal oxide of WO_3/SnO_2 in the soybean oil transformation in comparison with the individual WO_3 and SnO_2 species [306]. The bonding of WO_3 with SnO_2 was believed to upgrade WO_3/SnO_2 acidity. The catalyst is highly stable and was reused up to 4 times without much depreciation in the biodiesel yield.

Further, Xie *et al.* [307] studied 30 wt. % WO_3 loading on $AlPO_4$ catalyst and recorded a good 72.5 % conversion to biodiesel under the optimized reaction condition such as 30:1 M/O molar ratio, 5 wt. % catalyst loading, 180 °C temperature and 5 h reaction time. The high catalyst reactivity was attributed to the existence of WO_3 that enhanced the surface acid sites. Similarly, Amani *et al.* [308] reported a series of $Mn_{3.5x}Zr_{0.5y}Al_xO_3$ catalyst for the transformation of WCO to FAME. The $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalyst demonstrates better catalyst reactivity as far as FAME yield (>93 %) than the $Mn_{1.4}Zr_{0.35}O_3$ catalyst (52.8 %). The bonding between metals in the crystal structure efficiently influenced the catalyst reactivity. It was observed that the amphoteric component of the Al developed the surface region of the catalyst and framed a complex structure with other metal oxides, though Mn alternated the morphology and catalyst basic site density. In the meantime, Zhang *et al.* [309] reported Zr-Mo mixed metal oxide functionalized with various carboxylic acids, for example, lauric acid, stearic acid, palmitic acid and myristic acid for biodiesel production from oleic acid. The modification of Zr-Mo metal oxide using such monofunctional carboxylic acids enhances the catalyst acidity and surface area, thus upgraded the rate of the reaction. They also reported that among all, stearic acid-functionalized Zr-Mo metal oxide showed the best result with the maximum oleic acid conversion of 94. 2 %. Catalyst reusability test revealed that the catalyst is stable up to 6 progressive cycles. Similarly, WCO was utilized for the FAME production using ferric-manganese doped tungstate molybdena nanoparticles (FMWMo) [310]. The dopants Fe-Mn enhances the surface area, density of acidic sites and the stability towards the esterification of WCO. A maximum yield of 92.3±1.12 % methyl ester was achieved under the optimized reaction conditions.

Table 17: Different types of solid acid catalysts for FAME production.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1.	Fe_2O_3-SiO_2	Jatropha oil	218:1, 15, 220, 180	95.6	[302]
2.	$ZnA_{l2}O_4/ZnFe_2O_4$	Sunflower oil, WCO, Jatropha oil	9:1, 5, 180, 600	>90	[303]
3.	SnO_2-SiO_2	Soybean oil	24:1, 5, 180,300	81.7	[304]
4.	Fe-Mn-MoO_3/ZrO_2	WCO	25:1, 4, 200, 300	95.6 ± 0.15	[305]
5.	WO_3-SnO_2	Soybean oil	30:1, 5, 110, 300	79.2	[306]
6.	WO_3(30 wt. %)/$AlPO_4$	Soybean oil	30:1, 5, 180, 300	72.5	[307]
7.	$Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$	WCPO	14:1, 2.5, 150, 300	>93	[308]
8.	Zr-Mo	Oleic acid	10:1, 4, 180, 120	94.2^b	[309]
9.	FMWMo	WCO	25:1, 6, 200, 480	92.3±1.12	[310]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

8.2.2 Ion exchange resin

It is a well-known fact that several catalysts have been employed for FAME production from various feedstocks. But due to the certain disadvantages of conventional catalysts, researchers are always in search of an ideal catalyst which should overcome all associated limitations such as catalyst should be active at lower temperatures, exhibits high catalytic efficacy in terms of conversion of FAME, easy availability, low cost, easy downstream processing and reusability. Such an ideal catalyst can be considered as potential and economically viable candidates for biodiesel production [311]. In this context, one of them is ion exchange resin which meets most of the specifications of an ideal catalyst. Thus, many research groups have studied the role of ion exchange resins as solid catalysts in FAME production [312],[313]. Resin is the insoluble solid material that can retain and discharge ions simultaneously [314]. Resins are broad categories into cationic and anionic resin based on functional groups and degree of cross-linkages. It possesses specific functional groups responsible for the permutation of ions [314]. Having one of the important properties, the resin-based catalyst undergoes easy recovery from liquid mixtures by simple methods and are active at low temperature.

Since last few years, the cationic resins have gained considerable attention due to the advantages like functioning at soft reaction conditions, non-corrosive nature, more numbers of active sites and lower residual waters production [315],[316]. The cationic resin catalysts possess numerous active acid sites that play a crucial role in FAME production *via* esterification/transesterification reactions [316],[317]. Various ion exchange resin catalyst utilized for FAME production together with ideal reaction conditions are listed in Table 18. In 2007, Shibasaki-Kitakawa *et al.* [318] in a comparative study reported that cation exchange resins showed less efficacy than anion exchange resins towards the conversion of triacylglycerols to biodiesel. Moreover, while evaluating the conversion rates of various commercial resins such as Diaion PA308, PA306, PA306S and Diaion HPA25, it was observed that highly porous resin-like Diaion HPA25 showed low conversion rate and it is believed this might be due to resistance of the resin towards the water. According to Ren *et al.* [319] transformation of soybean oil to FAME reduced from 95.2 % to 87.7 % in the existence of D261 anion-exchange resin when the water content is enhanced from 0.0 % to 1.0 % by mass of oil. Similarly, in another study Deboni *et al.* [320] also reported lowering of reaction rate due to the presence of water inside the resins.

Generally, ion exchange resins are utilized for purification and softening of water at room temperature. Recently, Kansedo *et al.* [321] compared the catalytic efficiencies of different ion exchange resins like Amberlyst 15, Dowex DR-2030 and DR-G8 for the transformation of FFA into FAME *via* esterification of the sea mango oil (hydrolyzed) at RT. The results revealed that Amberlyst 15 showed maximum efficacy with the highest FAME production compared to Dowex DR-2030 and Dowex DR-G8. However, Jaya *et al.* [322] utilized ion exchange resins catalyst at a moderately lower temperature (50 ºC to 80 ºC) for biodiesel production which is analogous to those of homogenous catalytic process. Further, Umer and co-worker investigated the transformation of *Lagenaria Vulgaris* seed oil to biodiesel exploiting Amberlyst 15 resin and calcium oxide (egg cell) catalyst. The authors reported 93.2 % yield of biodiesel when Amberlyst 15 ion exchange resin was used as a catalyst with the loading of 5 % w/w and M/O ratio of 40 % w/w for 40 min of and reaction time at 60 ºC [323]. Similarly, Kansedo and Lee [324] investigated the esterification of hydrolyzed sea mango oil utilizing different cationic ion exchange resins, and over 80 % yield of FAME was recorded using Amberlyst 15 catalyst at a comparatively lower temperature within 1 hr of reaction time and with catalyst loading less than 5 % w/w.

Recently, Deboni *et al.* [320] reported 99 % yield of methyl and ethyl esters from soybean oil with methanol and ethanol respectively using alcohol/oil molar ratio of 16:1 and

Amberlyst A26 OH resin catalyst loading of 20 % w/w and reaction time of 6 h at 50 ºC temperature with stirring at 500 rpm. Whereas, Guzhan *et al.* [325] recorded 63 % yield of FAME from canola oil with oil to ethanol molar ratio of 6:1, Amberlyst-26 catalyst loading of 3.0 % w/w and reaction time 1.5 h at 45 ºC temperature with stirring at 1000 rpm. Moreover, in another study, a yield of about 67 % was observed for canola oil and methanol with almost similar reaction conditions [314,325]. The conversion of tallow fat with methanol showed the yield of methyl and ethyl esters around 95 % using Amberlyst-A26 OH with reaction conditions like tallow fat with methanol molar ratio of 6:1, resin loading of 2 mol/L at 65 °C temperature for about 8.5 hours [326].

Hartono *et al.* [327] investigated the catalytic efficacy of heterogeneous catalyst obtained from a different source like Lewatit macroporous resin, Amberlite gel resin and natural zeolite from Bayah to transform WCO to biodiesel. Authors reported the 85.94 % yield of biodiesel production by Lewatit macroporous anion exchanger with 6 M NaOH for 2 h at 60 °C with a ratio of M/O, 7:1 and 3 % by weight of catalyst loading. Whereas, Amberlite gel with 6 M HCl displayed 65.22 % biodiesel generation. Previously, Shibasaki-Kitakawa *et al* [328] reported the usefulness of the anion-exchange resin from their catalytic and adsorption abilities for the transformation of WCO to FAME. In their another study, Shibasaki-Kitakawa *et al.* [329] also developed ion-exchange resin catalysts based continuous process for the production of biodiesel. FFA conversions rate was estimated for different catalysts with reactions conditions like mole ratio of M/O (6:1), temperature (63.83 °C), reaction time (2 h) and catalyst load (20 wt. %). The maximum FFA conversions of 79.7 % were recorded for NKC-9. Whereas, for 001 x 7 and D61 catalysts it was found to be only 32.2 % and 10.3 % respectively [330]. Jalilnejad-Falizi *et al.* [331] achieved the highest FFA conversions by ion exchange resins (PD206-Na^+ and PD206-H^+) at the conditions of 20 wt. % of catalyst, at 65°C temperature for 48 h and 18:1 as M/O ratio. All the above-mentioned reports are enough to summarize that ion exchange resins can be employed as one the potential heterogeneous catalysts in biodiesel production.

Table 18: Different ion exchange resin catalyst used for the production of biodiesel.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1	D261 anion-exchange resin	Soybean oil	9:1, 50.15, 56	95.2^b	[319]

2	Amberlyst A26 OH anion exchange resin	Acid soybean oil	9:1, 2, 50, NR	78	[320]
3	Amberlyst-15	Hydrolyzed sea mango oil	6:1, 30,30, NR	>90	[321]
4	Basic anion exchange resin.	Pongamia oil	9:1, 75, 60	85	[322]
5	Amberlyst 15 ion exchange resin	Lagenaria vulgaris seed oil	40:1, 5, 60, 40	93.2	[323]
6	Amberlyst	Hydrolyzed sea mango oil	3:12, 100, 60	>80	[324]
7	Amberlyst-26	Canola oil	6:1, 3, 45, 90	67	[325]
8	Amberlyst-A26 OH	Tallow fat	6:1, 2 mol/L, 65, 360	95	[326]
9	Amberlite gel resin	WCO	7:1, 60, 120	85.94	[327]
10	Cation-exchange resin	Rice bran oil	6:1, 20, 63.83, 120	79.7	[329]
11	Purolite-PD206	Corn oil	18:1, 65, 2880	79.45	[331]

[a] Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).

[b] Conversion

NR: Not reported

PFAD: palm fatty acid distillate

8.2.3 Sulfated catalyst

Among solid acid catalysts, sulfated catalysts have attracted considerable attention for transesterification due to their super-acid property. Sulfated inorganic metal oxides are reported to be chemically stable, and have super acidity comparable to 100 % sulfuric acid, remarkable acid-base and redox properties [332]. Different kinds of sulfated catalysts such as sulfated zirconia, tin oxide, zirconia-alumina, etc. have been successfully exploited in the production of biodiesel; but among these, sulfated zirconia is most widely studied catalyst (Table 19). Various reports are available on the transformation of oil to FAME utilizing sulfated zirconia catalyst, but there are some studies which presented certain drawbacks of these catalysts which include low catalytic activities, drastic reaction conditions, and reusability issues. Moreover, lack of uniform pore size and low surface area are the other factors which restrict their wide uses in catalyzing bulky oil molecules of biodiesel feedstocks. In this context, several attempts have been made to modify sulfated zirconia catalysts with an intention to increase their catalytic efficacy.

Xia *et al.* [333] demonstrated the synthesis of mesoporous materials which has the potential to improve the activity of sulfated zirconia catalyst owing to their promising and outstanding properties like high surface area, uniform and controllable pore size. According to Alexander *et al.* [334], the modification of sulfated zirconia catalyst enhanced the total acidity which basically increased catalyst active sites. In another study, Guoliang *et al.* [335] proposed that change in phase structure of sulfated zirconia can also increase its catalytic activity and therefore, they developed tetragonal sulfated zirconia which showed enhanced catalytic activity in the FAME synthesis procedure. Moreover, some of the studies proposed the modification of sulfated zirconia on MCM-41 (Mobil Composition of Matter No. 41) support for the generation of methyl tert-butyl ether to improve its catalytic performance, the results obtained revealed that the catalytic performance of the prepared supported sulfated zirconia catalyst was 2.5-3.0 times greater than neat sulfated zirconia [333,336]. Similarly, Muthu *et al.* [337] reported the preparation of FAME from neem (*Azadirochta indica*) oil using sulfated zirconia catalyst. It was revealed that catalyst is highly stable to oils with high FFA concentration. The strong acid sites of this catalyst showed a considerable impact on its reactivity in the transformation of neem oil.

Recently, Lam *et al.* [338] developed SO_4^{2-}/SnO_2 catalyst by impregnation method and exploited it for the conversion of WCO to biodiesel. Further, the authors studied the bi-metallic impact of the catalyst, in which SnO_2 was blended in with SiO_2 and Al_2O_3, at various weight ratios to increase the activity of SnO_2. The finding confirmed that SO_4^{2-}/SnO_2-SiO_2 weight ratio of 3 showed exceptionally high reactivity with 92.3 % biodiesel yield utilizing catalyst loading of 3 wt. %, M/O ratio of 15:1 and reaction time 3 h at 150 °C. Similarly, Pereira *et al.* [339] demonstrated the application of $SnSO_4$ catalyst for the esterification of oleic acid (as model feedstock) and acid soybean oil having high contents of FFA. It was found that model feedstock containing 70 wt. % of FFA showed 92 % FAME yield using excess ethanol, 5 wt. % $SnSO_4$ at 100 °C for 3 h. Moreover, it was also reported that the catalyst is stable up to ten cycles without any significant decrease in biodiesel yield. Moreover, one of the studies involved the application of sulfated tin oxide modified with SiO_2 (SO_4^{2-}/SnO_2-SiO_2) catalyst to produce FAME from JCO. It was reported that 97 % FAME conversion was obtained at 180 °C, reaction period of 2 h, and M/O molar ratio of 15:1 [340]. The sulfated titania-based solid superacid catalysts are another kind of sulfated catalysts. Li *et al.* [341] prepared three different titania-based solid superacid catalysts and these were exploited for the transformation of rape seed oil to FAME at 353 K with a 12:1 molar ratio of M/O under atmospheric pressure. It was found that all three prepared catalysts showed a significant yield of biodiesel due to their stronger surface acidities. Moreover, Alaba *et al.* [332] reviewed that apart from these there are various other sulfated metal oxides such as titania, silica and combination of both also showed remarkable performance. It was also proved thorough investigation led by several researchers who have applied sulfated silica as catalysts for esterification and transesterification [342,343]. In this context, Gardy and co-workers demonstrated a facile preparation of sulfated doped TiO_2 catalyst that has been utilized efficiently in petroleum refinery. The authors reported that the synthesized catalyst has better reactivity than other sulfated metal oxides, primarily because of the acidic properties of TiO_2 particles, which was subjected to sulfonation to enhance its acidity. The catalyst displayed great efficiency in the synthesis of FAME from WCO [344],[345].

Table 19: Different types of sulfated catalyst reported for biodiesel production.

No.	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1	SO_4^{2-}/ZrO_2	Neem oil	9:1, 1, 65, 120	95	[337]
2	SO_4^{2-}/SnO_2-SiO_2	WCO	15:1, 3, 150, 180	92.3	[338]
3	$SnSO_4$	Soybean oil	3.5:1, 5, 100,180	92	[339]
4	SO_4^{2-}/SnO_2-SiO_2	Jatropha oil	15:1, 3, 180, 120	97	[340]
5	SO_4^{2-}/TiO_2	Rapeseed oil	12:1, NR. 80, 720	51	[341]
6	$Ti(SO_4)O$	WCO	9:1, 1.5, 75, 180	97.1	[344]
7	$TiO_2/PrSO_3H$	WCO	15:1, 4.5, 60, 540	98.3	[345]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (°C), reaction time (min).
NR: Not reported

8.2.4 Sulfonated carbon-based catalyst

In the last few decades, various carbon materials with different shape, size, and structures have been developed by several research groups and utilized as low-cost catalysts for diverse industrial processes including transesterification [346]. Currently, sulfonated carbons i.e. SO_3H-functionalized acidic carbon materials are considered as a new group of the metal-free solid acid catalyst described by their original carbon structure and Brønsted acidity equivalent to concentrated H_2SO_4. Sulfonated carbon acid catalysts can be easily prepared by processes like incomplete carbonization of aromatic compounds in concentrated H_2SO_4 [347]

or sulfonation of incompletely carbonized natural organic matter, such as sugar [348],[349],[350] and cellulosic materials [351],[352]. Sulfonation can also be achieved by treating carbon material with a sulfonating reagent such as gaseous SO_3, $ClSO_3H$, p-toluenesulfonic acid, 4-benzenediazonium sulfonate or SO_3H-containing aryl diazoniums etc. [347],[353],[354],[355],[356].These materials possess promising features such as biogenic, environment-friendly, lower production costs, distinctive surface chemistry, high chemical and thermal stability.

The acid-catalyzed chemical reactions such as saccharification, esterification, transesterification and acetylation are vital operations commonly used for the valorization of biomass or their components to useful products in various food, fuel and chemical industries [357]. The functionalized acidic carbons from inexpensive sources including natural organic carbon matter such as sugars, carbohydrates, cellulosic materials, lignin have been achieved by several researchers [358],[359],[360],[361]. Besides this, agro waste such as husk, straw, seed cover, cow manure, corn cob [362],[363] ,[364],[365], carbonaceous waste from industries (char, oil pitch, coke, glycerol, etc.) [353],[354],[366],[367],[368] and polymer resins [369],[370],[371] were also used. Various carbon supports (e.g. zeolite-templated carbons, mesoporous carbons, active carbon, etc) [372],[373],[374],[375] and more recently nanostructured carbons such as graphene, graphene oxide, carbon nanotubes, and carbon dots) [376],[377],[378],[379],[380],[381] have been exploited for the same purpose.

Over the last few years, there is growing interest from researchers towards the application of sulfonated carbon-based catalysts due to their noteworthy efficacies mentioned earlier. Many reports are available which demonstrated the efficient nature of sulphonic acid-functionalized catalyst in biodiesel production using various feedstocks [382],[353],[383]. One of the reports presented the synthesis of organosulfonic acid (i.e. propylsulfonic and arenesulfonic groups) functionalized mesoporous silicas through a simple one-step process. The synthesized novel catalysts that possessed propylsulfonic groups and arenesulfonic groups were further evaluated for their catalytic efficacy in the esterification of fatty acid with methanol to produce methyl esters and the authors also compared the efficacy of these heterogeneous catalysts with a variety of commercially available catalysts such as sulfuric acid, p-toluene sulfonic acid, Nafion NR50, Amberlyst-15, etc. The obtained results indicated that the organosulfonic acid-functionalized mesoporous silica catalysts showed the highest reactivity compared to all the above mentioned commercial solid acid catalysts in fatty acid esterification process. Moreover, it was also recorded that the efficiency of these catalysts was largely depended on important factors such as the median pore diameter of the catalyst and the acidic strength of the organosulfonic acid group present over this catalyst. Considering these findings, it can be proposed that there is a huge potential to developed catalysts using organic-inorganic mesoporous materials [384]. In general, the activity of carbon-based catalysts upon fatty acid (C16-C18) esterification to produce biodiesel primarily depends on three primary factors: (i) -SO_3H group density, (ii) total acid density, and (iii) porosity. Different sulfonated carbon-based acid catalyst utilized for FAME production are listed in Table 20. Numerous reported catalysts demonstrated promising outcome in the (trans)esterification of biodiesel feedstocks with high FFA and afforded $> 85\%$ FAME yield. In the meantime, several investigations had been conducted using model acids (e.g. palmitic acid, oleic acid, etc. which are the major components of vegetable oil as reactant) that mainly focused on esterification reaction.

In a pioneering work towards the preparation of biomass-based sulfonated carbon catalyst, Toda *et al.* [385] synthesized sulfonated carbon catalyst by partial carbonization of sugar followed by sulfonation in fuming H_2SO_4. The prepared catalyst consists of sheets of indistinctive carbon having a high amount of sulfonic groups along with hydroxyl and carboxyl as a minor group (Figure 32). The highly active bio-based carbon catalyst was utilized for transformation of oleic and stearic acid to FAME *via* esterification. Apart from -SO_3H group, presence of -OH and -COOH groups in the catalyst greatly enhance the catalytic activity and make it highly water tolerant. The successful incorporation of –SO_3H group and formation of carbonized materials are can be easily confirmed by using FT-IR and ^{13}C MAS NMR analysis respectively, as depicted in Figure 33 [350]. FT-IR spectra (Figure 33a) displayed two bands at 1040 and 1377 cm^{-1} (in SO_3H), ascribed to SO_3 and O=S=O stretching vibration, respectively, suggests the existence of -SO_3H groups. ^{13}C MAS NMR (Figure 33b) depicted three major peaks at 130, 155, and 180 ppm, ascribed to polycyclic aromatic carbon atoms, phenolic OH, and COOH groups, respectively.

In another work, Hara *et al.*[353] examined sulfonated carbon catalyst in biodiesel synthesis. The findings showed that amorphous carbon material containing sulfonic acid groups enhances the catalytic performance, thus displayed extraordinary reactivity in esterification/transesterification reactions in comparison to the ordinary solid acid catalyst.

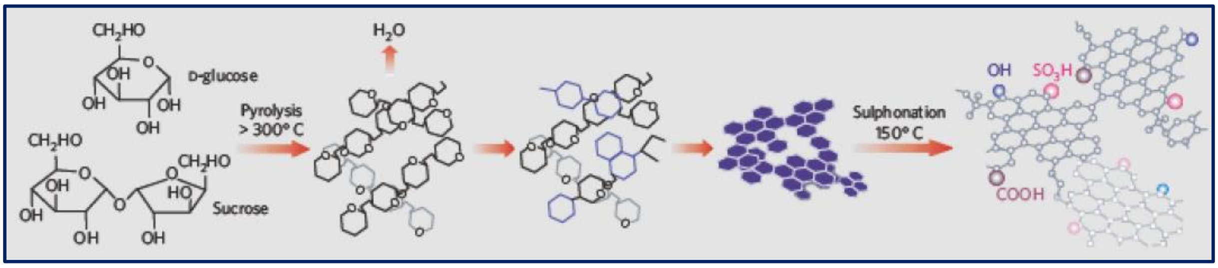


Figure 32: Synthesis of sulfonated carbon catalyst from sucrose and D-glucose. Adapted from ref. [385].

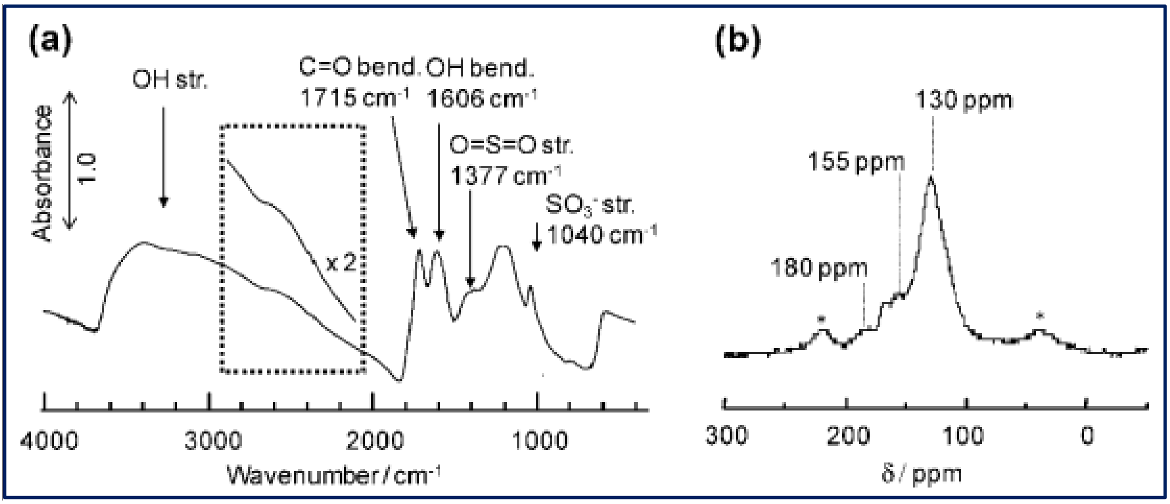


Figure 33: FT-IR (a) and 13C MAS NMR (b) spectrum for the sulfonated carbon catalyst originated from cellulose. Adapted from ref. [350].

Likewise, Nakajima *et al.*[386] synthesized amorphous cellulose-originated carbon solid acid (CCSA) catalyst and exploited it in the transformation of oleic acid to FAME, and observed a 99.9 % yield under the optimized conditions. The carbon material displayed much higher catalytic activity in esterification reaction in comparison to ordinary solid acid catalysts examined, such as niobic acid, Amberlyst-15 and Nafion NR50. Interestingly, those CCSA catalyst prepared at a lower carbonization temperature before subjected to sulfonation gave a lot better biodiesel yield as compared to those prepared at higher carbonization temperature. This is attributed to the huge amount of –OH and –COOH groups in the former which enhanced its acidic nature, thereby its catalytic activities (Figure 34). The catalyst reactivity remains intact after 10 progressive cycles.

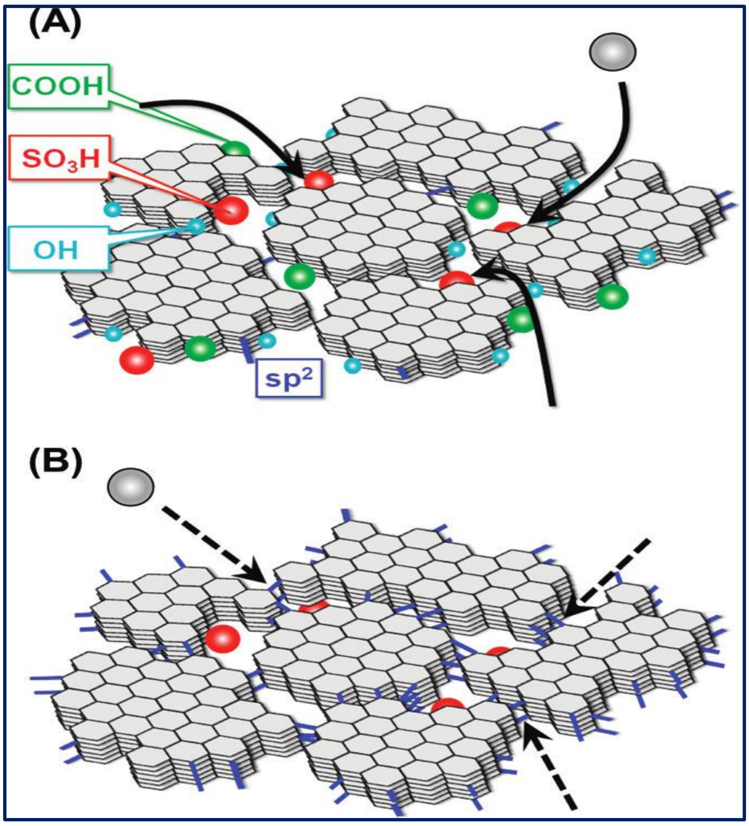


Figure 34: Schematic structures of SO_3H-bearing CCSA materials carbonized at below 723 K (A) and (B) above 823 K. Adapted from ref. [386].

Simultaneous carbonization and sulfonation in a one-pot synthesis of solid acid catalyst directly from biomass have also been explored by various experts as it is straight forward, cost and time-efficient. Malins *et al*. [387] synthesized C-SO_3H via simultaneous carbonization-sulfonation and utilized it for FAME production. The C-SO_3H catalysts with the highest density of SO_3H groups (0.81 mmol Hþ/g) were prepared using reaction conditions like a molar ratio of H_2SO_4 to cellulose 20/1, temperature 100 ˚C and reaction time of 180 min. It was noted that under optimized reaction conditions 96.5 % of FAME was recorded. Interestingly, the catalyst has great stability and can be easily recovered and reused for subsequent reaction cycles. Moreover, in the comparative study of esterification reactions of rapeseed oil fatty acids, the prepared catalyst exhibited similar reactivity to Amberlyst-15.

Another recent report proposed a synthesis of the heterogeneous sulfonated catalyst using activated carbon to overcome several problems like drastic reaction conditions such as very high temperature, pressure, longer reaction time and expensive overall process cost. The above-mentioned activated carbon catalyst was prepared from corncobs as a precursor and utilized in the microwave-assisted conversion of soybean oil with ethanol to FAME. In this study, about 88.7 % yield of pure biodiesel was reported at 0-600 W of microwave power for 20 min, alcohol-to-oil molar ratio of 6:1 and catalyst concentration of 20 wt. %. Moreover, the catalyst was reused up to 5 cycles [365]. Figure 35 represents the schematic illustration of the application of activated carbon-based catalyst in the transesterification of various oils using methanol.

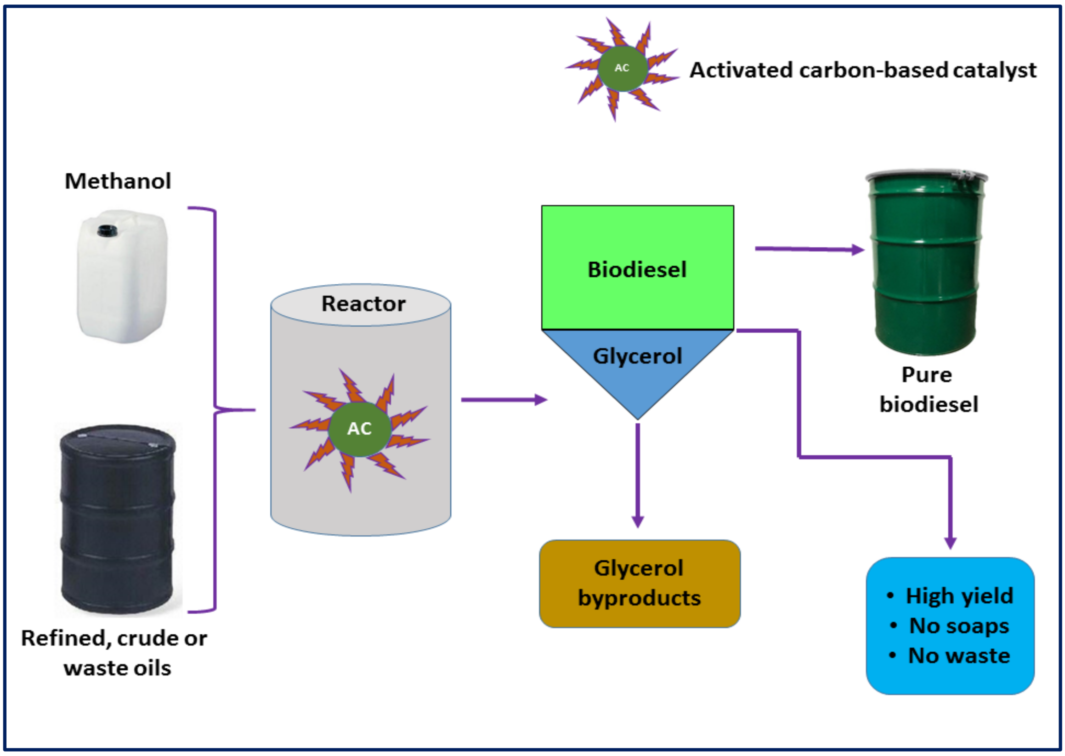


Figure 35: Schematic representation of transesterification of various oils using activated carbon-based catalysts.

In 2009, Yuan *et al.* [388] examined the application of solid acid catalyst originated from sulfonated activated carbon (H_2SO_4/C) for catalyzing transesterification of castor oil and methanol as feedstock. Melero *et al.* [389] synthesized sulfonic acid-modified mesostructured (SAM) catalyst and studied their efficacy in crude vegetable oils transformation to FAME. The results obtained noted that this catalyst has the ability to yield 95 wt. % pure FAME and oil transformation close to 100 %. Despite the presence of FFAs, this catalyst displayed significantly high activity toward simultaneous esterification and transesterification reactions. Similarly, Zuo *et al.* [390] developed various sulfonic acid functionalized mesoporous SBA-15 catalysts and tested their catalytic activity in the microwave-assisted conversion of soybean oil and 1-butanol to biodiesel. The authors observed that the catalytic efficacy of these catalysts mainly depends on the acid strength and not on the number of acid sites. Further, propyl-SO_3H and arene-SO_3H functionalized SBA-15 catalysts found to have comparatively better reactivity in the transesterification process. However, perfluoro-SO_3H functionalized SBA-15 catalyst displayed leaching of the active sites in each progressive cycles, thus reactivity decreased. Shah *et al.* [391] demonstrated esterification of FFAs in acid oil (which is a byproduct of oil refining) using sulfonic acid-functionalized silica (SiO_2–Pr–SO_3H) catalyst to prepare biodiesel. Further, the authors optimized various reaction conditions such as temperature, reaction time, catalyst concentration, and M/O molar ratio, etc. which usually affects the conversion to FAME. A high conversion (i.e. 96.78 % conversion after 8 h was reported at optimized conditions) can be achieved using these solid acid catalysts.

Moreover, in recent past Varyambath *et al.* [392] developed different sulfonic acid-functionalized organic knitted porous polyaromatic microspheres (OPPSO_3H) utilizing pyrene, anthracene, and naphthalene as monomers *via* Friedel-Crafts alkylation, followed by crosslinking reactions. Further, these heterogeneous catalysts were utilized for the transformation of long-chain fatty acids and triglycerides to biodiesel. These solid acid catalysts were found to be very promising for biodiesel synthesis as they showed excellent surface acidity. In addition, several other sulphonic acid-functionalized catalysts were successfully developed and exploited in the production of biodiesel. In this context, Shagufta *et al.* [393] reviewed all such sulphonic acid-functionalized in catalysts esterification and transesterification reactions. This review can be consulted for more detail information.

Yu *et al.*[394] studied biodiesel production by exploiting coal-based acid catalysts and reported an oleic acid conversion of 97.6 % under the optimal reaction conditions like methanol/oleic acid molar ratio of 10:1, 8 wt. % catalyst concentration, temperature 67°C and reaction time of 240 min. Similarly, Tang and Niu [395] investigated the synthesis of carbon-based solid acid catalysts from bamboo through partial carbonization and sulfonation approach. The microstructure of catalyst was activated by phosphoric acid impregnation. The catalyst afforded biodiesel yield 97.3 % at optimum conditions which decreased to 83.7 % in fourth reaction cycles. In addition, biodiesel production from oleic acid was reported using sulfonated activated carbon from bamboo [396]. A sulfonated carbonaceous material synthesized via single-step hydrothermal sulfonation of glucose has also been used as a catalyst for esterification of waste cooking oil to produce biodiesel [397]. FESEM images of the carbonaceous material (C) (Figure 36a) and the sulfonated carbonaceous material (C-SO_3H) (Figure 36b) showed microsphere and microsphere with an attached sulfonic group on the surface respectively. The catalyst showed great stability with 93.4 % FAME yield under the optimized reaction conditions.

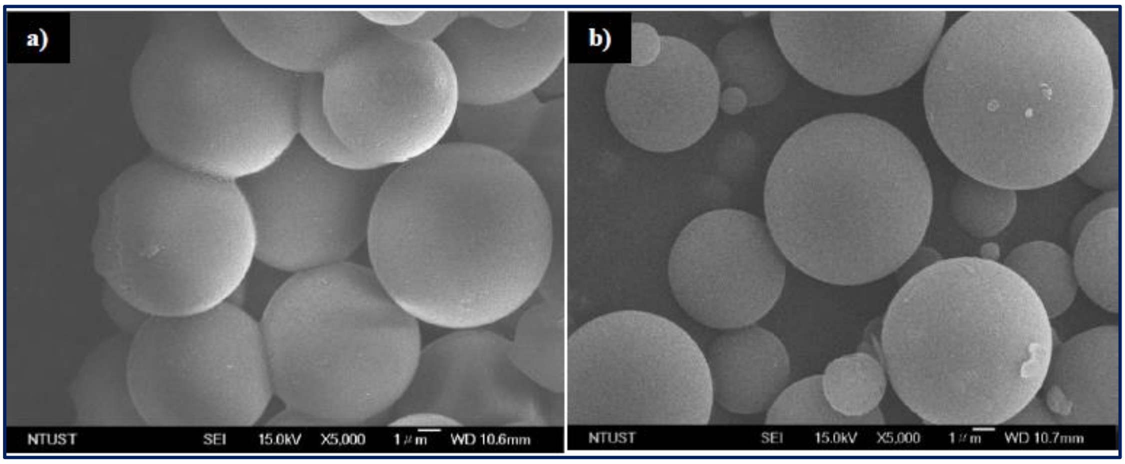


Figure 36: FESEM images of a) C and b) C-SO3H. Adapted from ref. [397].

Guan *et al.* [398] synthesized sulfonated multi-walled carbon nanotube (S-MWCNT) for the conversion of triglyceride to FAME in 97.8 %. The high catalytic reactivity is because of high surface area (198.9 m^2 g^{-1}), high porosity (10-15 nm) and high acid sites. Similarly, sulfonated carbonaceous material from starch was utilized as a solid catalyst for esterification of PFAD [399]. A novel, efficient, inexpensive and environment-friendly acid catalyst was synthesized from coconut meal residue (CMR). CMR-DS-SO_3H catalyst was prepared by a one-step direct in-situ carbonization in concentrated H_2SO_4 and reported for the transformation of waste palm oil (WPO) to biodiesel. The prepared sulfonated catalyst has acid density 3.8 mmol/g, surface area 1.33 m^2/g and means pore volume 0.31 cm^3/g. The results obtained recorded a high yield of 92.7 % biodiesel from WPO [400]. Moreover, Wang *et al.* [401] investigated the application of monodispersed hollow carbon/silica solid acid catalyst HS/C-SO_3H, which was prepared by chemical activation approach, in the esterification of oleic acid with methanol to produce biodiesel.

Besides this, another kind of sulfonated functionalized carbon material i.e. sulfonated ordered mesoporous carbon (SOMC) catalyst showed promising biodiesel production (73.59 % yield) [402]. Recently, sulfonated acid catalyst obtained from corncob (SO_4^{2-}/corncob), has been reported as an excellent catalyst for conversion of oleic acid to obtain methyl oleate in good yield (> 80 % after 8 h at 60 °C) [403]. Mahdavi and Darabi [404] prepared sulfonated carbon catalyst by treatment of sucrose and concentrated H_2SO_4 at high temperature (sulfonation and carbonization approach). The synthesized C-SO_3H catalyst was further utilized for the conversion of oleic acid to FAME in 93.04 % yield. Moreover, a solid acid catalyst generated from sulfonation of microcrystalline cellulose powder was successfully applied for oleic acid esterification, showed 99.9 % biodiesel yield under the optimized reaction conditions [405]. In another investigation, waste cooking oil was transformed to produce biodiesel utilizing an environmentally benign sulfonated carbon microsphere catalyst [406]. The catalyst with surface area 86 m^2/g and acidity 1.38 mmol/g was developed by consecutive hydrothermal carbonization and sulfonation of xylose. Using this catalyst, biodiesel yield of 89.6 % was recorded at reaction conditions of a temperature of 110 °C, time 240 minutes, catalyst loading of 10 wt. % under elevated pressure of 2.3 bar for first and 1.4 bar for the second step. Catalyst reusability report revealed that in each cycle biodiesel yield was reduced by 9 %. Furthermore, sulfonated carbon-based solid acid catalyst was also utilized for the transformation of PFAD [407] and *Mesua Ferrea* Linn oil [408] to biodiesel.

To bring down the cost of biodiesel production, several sulfonated raw biomass has been prepared and investigated for their catalytic activities. In this line, a sulfonated solid-acid catalyst obtained from coconut shells (SO_4^{2-}/coconut shell) reported 88.03 % biodiesel yield [409]. In the same vein, oil palm trunk/ sugarcane bagasse [410], corn straw [411], bamboo [412], Jatropha curcas seed [413], bio-glycerol [414], glycerol [415] microalgae residue [416], oil cake waste [417],[418], de-oiled waste cake [419], de-oiled canola meal-SO_3H [420] pine chip char [421] and biochar [422],[423] are reported as a catalysts for FAME production.

Table 20: Different sulfonated carbon-based acid catalyst used for biodiesel production.

No.	Catalyst	Feedstock	^{a}Conditions	Yield (%)	Ref.
1.	Sulfonated sugar	Oleic acid	10:1^f, 7.4, 80, 240	NR	[385]
2.	Sulfonated carbon	Oleic acid	2.92:1^c, 17.2, 95, 240	99.9	[386]
3.	ACPhSO_3H	Rapeseed oil	20:1, 10, 65, 420	95	[387]
4.	Sulfonated AC	Soybean oil	6:1, 20, 75, 20	88.7	[365]
5.	H_2SO_4/C	Castor oil	12:1, 5, 65, 60	94	[388]
6.	SAM	Vegetable oil	10:1, 6, 180, 120	95	[389]
7.	SO_3H/SBA-15	Soybean oil	6:1, 5, 190, 30	90	[390]
8.	SiO_2–Pr–SO_3H	Acid oil	15:1, 4, 100, 480	96.78^b	[391]

9.	OPPSO$_3$H	Soybean oil	50:1^{c}, 10, 70, 600	93^{b}	[392]
10.	Coal based solid acid	Oleic acid	10:1, 8, 240, 67	97.6^{b}	[394]
11.	Sulfonated carbon-based solid acid	Oleic acid	10:1,10,65, 120	97.3	[395]
12.	Sulfonated activated carbon	Oleic acid	7:1^{f}, 12, 180, 85	96^{b}	[396]
13.	C-SO3H	Waste cooking oil	20:1, 10, 60, 180	93.6	[397]
14.	Sulfonated multiwalled carbon nanotube	Triglycerides	10:1^{f}, 3.7, 60, 150	97.8^{b}	[398]
15.	ICS-SO3H	Palm fatty acid distillate	10:1, 2, 180, 75	90.4	[399]
16.	CMR-DS-SO$_3$H	Waste palm oil	12:1, 5, 65, 72	92.7	[400]
17.	HS/C-SO$_3$H	Oleic acid	5:1, 3.5, 80, 300	96.9^{b}	[401]
18.	SOMC	Oleic acid	10:1, 3.5, 80, 600	73.59^{b}	[402]
19.	SO$_4^{2-}$/corncob	Oleic acid	15:1, 5, 60, 480	>80	[403]
20.	C-SO$_3$H	Oleic acid	10:1, 1.5, 67, 120	93.04	[404]
21.	C-SO$_3$H	Oleic acid	16:1, 17, 95, 240	99.9	[405]
22.	C-SO$_3$H	WCO	10:1, 10, 110, 240	89.6	[406]
23.	C-SO$_3$H	PFAD	15:1, 2.5, 80, 240	95.3^{b}	[407]
24.	C-SO$_3$H	*Mesua Ferrea* Linn oil	40:1, 5, 120, 1440	97.79	[408]
25.	Coconut shell-SO$_3$H	Palm oil	30:1, 6, 60, 360	88.03	[409]
26.	Oil palm trunk/	Waste Oil	1.17 mL/min, 12, 130, 240	80.6/83.2	[410]

	Sugarcane bagasse-SO$_3$H				
27.	Corn straw-SO$_3$H	Oleic acid	3:1, 3, 60, 240	92	[411]
28.	Bamboo-SO$_3$H	Oleic acid	7:1^f, 2, 90, 360	98.4	[412]
29.	Jatropha curcas Seed-SO$_3$H	JCO	12:1, 7.5, 60, 60 99.13	99.13^b	[413]
30.	Bio-glycerol	Karanja oil	45:1, 20, 160, 240	99.5	[414]
31.	Glycerol	Palmitic acid	9.7:1^c, 10, 65, 240	99^b	[415]
32.	Microalgae residue	Oleic acid	NR,5, 80, 720	98^b	[416]
33.	Oil cake waste-SO$_3$H	JCO/ *M. ferrea* L. oil	43:1, 5, 80, 480	99	[417]
34.	Oil cake waste-SO$_3$H	Oleic acid	12:1, 20, 60, 120	94^b	[418]
35.	De-oiled waste cake	Oleic acid	20:1, 3, 64, 600	97^b	[419]
36.	De-oiled canola Meal-SO$_3$H	Oleic acid	60:1, 7.5, 65, 1440	93.8^b	[420]
37.	Pine chip char	Palmitic acid	6:1, 5,55-60, 300	97	[421]
38.	Biochar	Canola oil	15:1^f, 5, 65, 1440	92	[422]
39.	Biochar	Canola oil, oleic acid	30:1, 5, 315, 180	48	[423]

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[a] Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

[b] Conversion

[f] Ethanol to oil molar ratio

NR: Not reported.

8.3. Bifunctional solid catalysts

Despite the high reactivity of the basic solid catalyst towards biodiesel production, they are not an effective catalyst for transesterification of oils having a high amount of FFA as such catalyst are highly sensitive to the FFA, which leads to soap generation and thus interfere in the separation process of glycerol from biodiesel. On the other hand, solid acid catalysts are insensitive to the FFA content and esterify waste oils or low-cost oils without any requirement of pretreatment. However, water formed during the course of the reaction may lead to the decomposition of triglycerides to diglycerides, resulting in the formation of more FFA and catalyst leaching. Taking these difficulties into account, developing a new type of solid catalysts that possess dual characteristics such as solid acidic character to tackle the FFA and solid basic character for easy transesterification of triglycerides to FAME has been a recent interest in the realm of biodiesel research. To date, numerous bifunctional catalysts are reported for the FAME production (Table 21), which will be discussed in this section. Farooq *et al.* [424] developed a bifunctional Mo-Mn/γ-Al_2O_3-MgO catalyst and utilized it for the simultaneous esterification/transesterification of WCO having FFA content of 3.27 mg KOH/g. The authors investigated the effect of MgO loading (5-20 wt. %) on its catalytic activity and found that 15 wt. % MgO loading showed highest catalytic activity with 91.4 % biodiesel yield under the ideal reaction conditions. Moreover, the catalyst showed excellent stability towards the biodiesel production from WCO as it is stable up to 8 progressive reaction cycles without any major loss of its activity. In another study, Cu/Zn/γ-Al_2O_3 catalyst was utilized for the simultaneous esterification/transesterification of WCO for production of FAME via RSM [425]. The effect of Cu/Zn wt. % ratio and calcination temperature on the catalytic reactivity was also examined and found that 10:90 Cu/Zn wt. % ratio and 800 °C calcination temperature showed 88.82 % FAME yield. The authors also studied the structure and particle size of the synthesized catalyst *via* TEM micrographs (Figure 37). Figure 37a displayed that the average diameter of the particles lies in between 4-6 nm. The lattice fringes measured from Figure 37b, c and d are 0.201, 0.282 and 0.242 nm, matched with the hkl planes (400), (220) and (311) of alumina respectively. The lattice fringes in Figure 37e is 0.240 nm fitted with the hkl plane (200) of CuO and lattice fringes 0.281 nm (Figure 37f) fitted with the ZnO plane (100). Similarly, biodiesel production from WCO was reported using diverse bifunctional solid catalysts such as Mg/MCM-41[426], γ-Al_2O_3-CeO_2 [427], KAcZX [428] and Sr/ZrO_2 [429]etc.

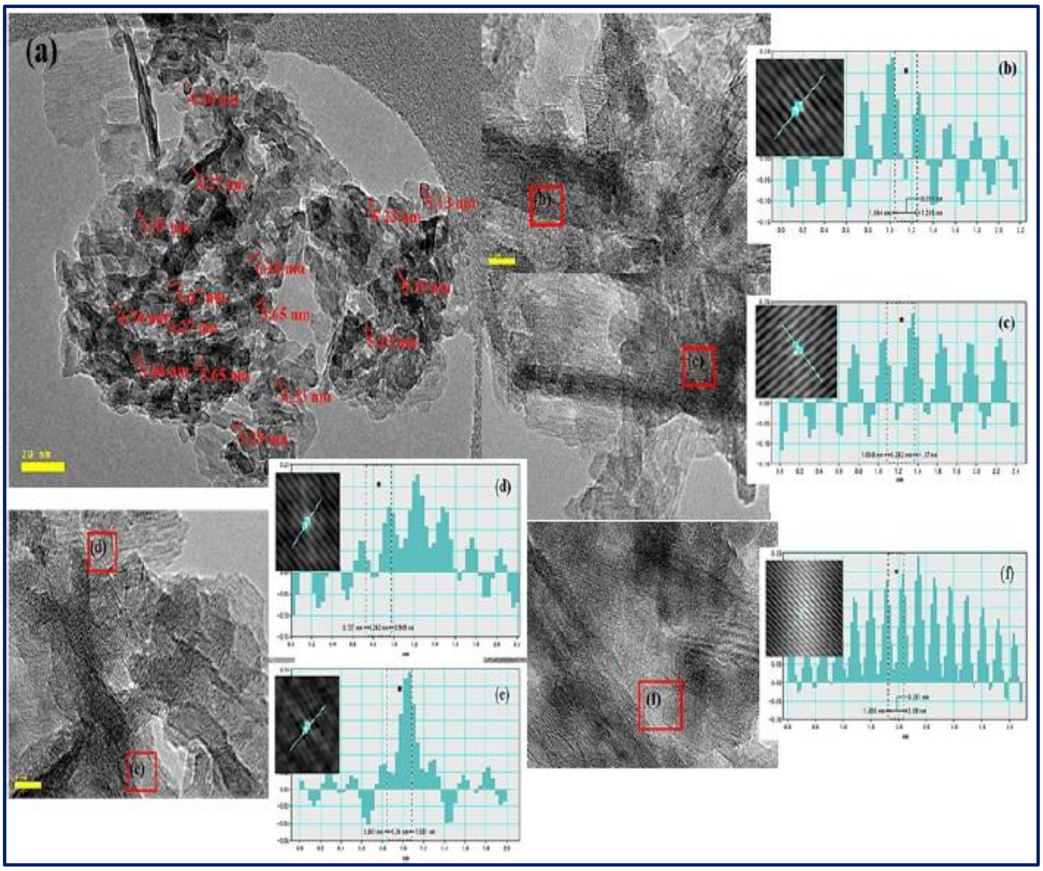

Figure 37: TEM micrograph for Cu/Zn(10:90)/γ-Al_2O_3-800 °C (a) HRTEM displayed the lattice fringes of (b) Al_2O_3 (400), (c) Al_2O_3 (220), (d) Al_2O_3 (311), (e) CuO (200) and (f) ZnO (100). Adapted from ref. [425].

Nizah *et al.* [430] synthesized a bifunctional catalyst Bi_2O_3-La_2O_3 *via* wet impregnation procedure and employed it for one-pot esterification/transesterification of JCO having FFA content of 6.1 mg KOH/g. The authors investigated the influence of Bi_2O_3 impregnation on La_2O_3 support by varying the wt. % of Bi_2O_3 in the range of 1-7 wt. % and found that 5 wt. % Bi_2O_3 impregnated on La_2O_3 showed maximum biodiesel yield of 94 %. The high catalyst reactivity is attributed to the well dispersion of Bi_2O_3 on La_2O_3 support, that directly enhanced the surface area and thus increases selectivity and rate of the reaction. Similarly, biodiesel production from JCO having a high amount of FFA was reported by using a bifunctional solid catalyst CaO-La_2O_3 [431]. The esterification/transesterification was performed in a high-temperature reactor (Figure 38). The effect of Ca/La atomic ratio on the catalytic activity was examined and observed that 0.8 atomic ratio of Ca/La showed maximum biodiesel yield of 98.76 % under the optimized reaction conditions. The high catalytic reactivity is because of well dispersion of CaO on the surface of La_2O_3, that led to an increase in catalyst surface area. Moreover, the synthesized catalyst is chemically stable and can be used for 4 consecutive cycles.

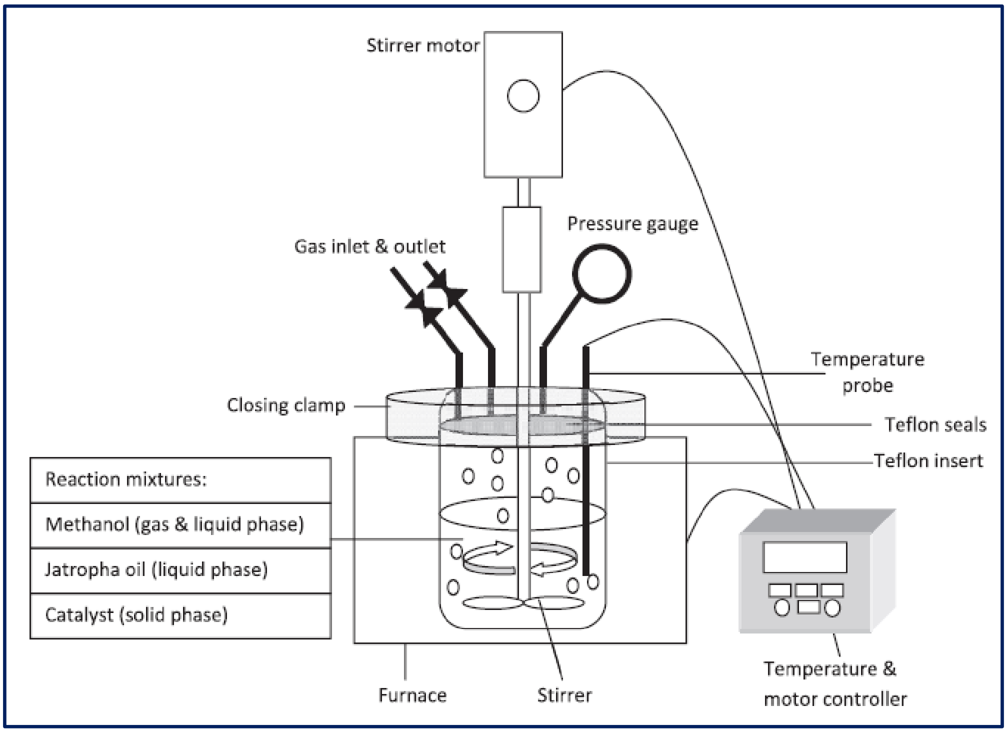

Figure 38: Schematic diagram of a high-temperature reactor. Adapted from ref. [431].

Another study revealed the synthesis of mixed metal oxide Mn@MgO-ZrO_2 via co-precipitation and impregnation method and utilization of the catalyst in the FAME production from kernel oil [432]. The efficiency of the catalyst in FAME production was tested by changing the Mg/Zr ration from 0.2-05 and found that 0.4 Mg/Zr has the optimal active sites followed by impregnation of 4 wt. % Mn to MgO-ZrO_2 composite to enhance its reactivity and displayed 96.4 % biodiesel yield. The high catalyst reactivity is due to a large number of active sites and the mesoporous nature of the catalyst. Jeon *et al.*[433] synthesized heteropolyacid (HPA) functionalized ZIF-8 (zeolite imidazole framework-8) to form a bifunctional catalyst for the production of biodiesel from rapeseed oil in a batch reactor. The catalyst possesses core-shell nanostructure as displayed by the TEM micrograph (Figure 39), where the rhombic dodecahedral ZIF-8 core was surrounded by thin-wrinkled HPA shell, thus enhances the surface area and catalyst reactivity. The possible chemical bonding between the HPA and ZIF-8 is displayed in Figure 40. Moreover, the effect of concentration of HPA for the functionalization was also tested by varying the amount of HPA such as 0.05, 0.1, 0.3 and 0.5

and found that 0.1 g HPA functionalized ZIF-8 showed maximum FAME conversion of 98.02 % under the optimized reaction conditions. Similarly, another bifunctional catalyst organotriphosphonic acid-functionalized ferric alginate (ATMP-FA) was developed for the oleic acid esterification to produce biodiesel [434]. The reaction conditions are optimized by using Box–Behnken model of RSM and found that 8.62:1 methanol/oleic acid molar ratio, 9.53 wt. % catalyst loading, reaction temperature of 91 °C and 600 min reaction time are the optimized reaction conditions under which maximum FAME conversion of 93.17 % has been achieved. Moreover, the catalyst is very stable towards the esterification reaction and can be reused for 5 consecutive cycles.

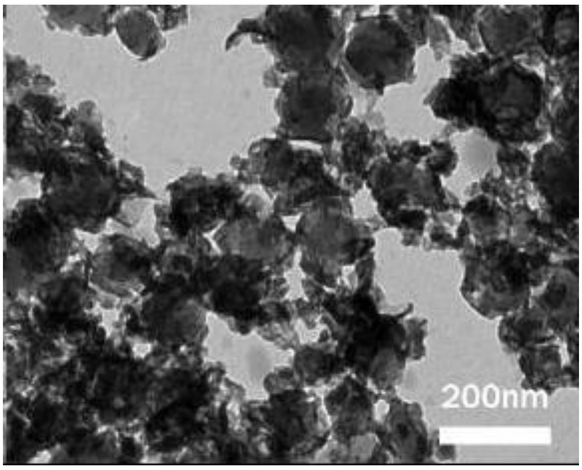

Figure 39: TEM image of HPA-ZIF-8. Adapted from ref. [433].

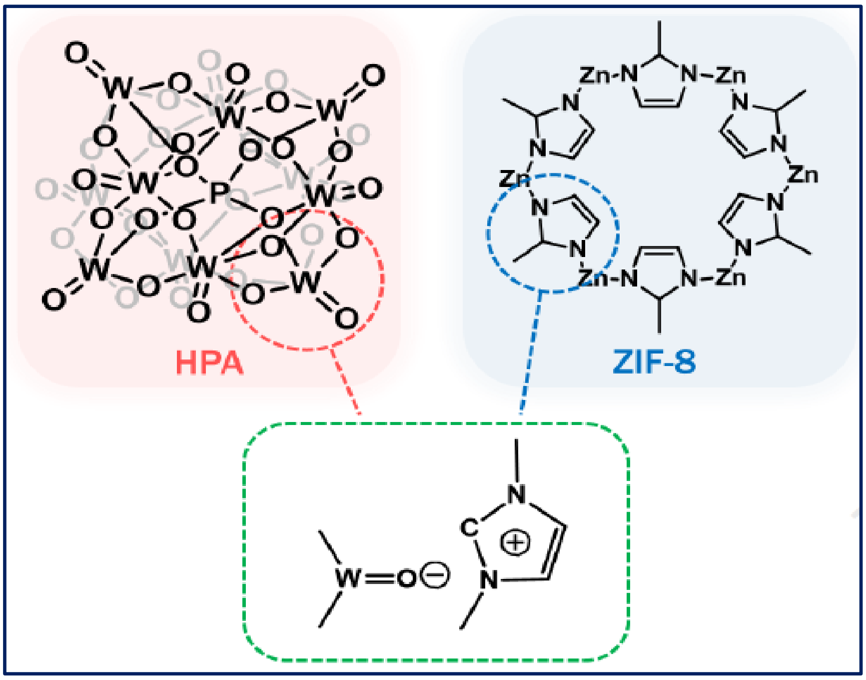

Figure 40: Possible chemical bonding between HPA and ZIF-8. Adapted from ref. [433].

Recently, a solid bifunctional catalyst originated from bio-waste angel wing shell (AWS) via two-step processes-i) calcination of angel wing shell and ii) sulfonation of the calcined angel wing shell to produce sulfonated angel wing shell (AWS/SO_4^{2-}) was reported for esterification of PFAD to produce biodiesel [435]. The sulfonation procedure increases the surface area of bare AWS from 3.88 to 6.53 m^2g^{-1}, thus enhanced the catalytic reactivity. The authors tested the influence of sulfuric acid concentration by varying the sulfuric acid amount from 3-11 M and found that sulfonation with 7M sulfuric acid showed 98 % FAME yield. The authors also checked the reusability of the catalyst and observed blockage of the active sites of the catalyst after 2nd consecutive cycles; which necessitate pretreatment of the spent catalyst to increase its reusability. In addition, a coordinated polymer of Zn, $[Zn(4,4'\text{-bipy})(OAc)_2]_n$ was tested for the soybean oil transformation to FAME [436]. The catalyst showed excellent reactivity and showed 98 % FAME yield under the optimized reaction conditions. The authors reported that the high reactivity of the catalyst is attributed to the bipyridine present in the catalyst. In another study, the conversion of canola oil to FAME was reported using potassium impregnated titania (K/TiO_2) [437]. The addition of K on the surface of titania increases the surface energy from 86 to 102 m^2/g, thus enhanced the catalytic activity. The authors investigated the effect of K loading on catalytic activity and found that 20 wt. % K loaded titania was optimum and showed 100 % conversion of canola oil to biodiesel.

Table 21: Different bifunctional solid catalyst reported for biodiesel production.

No	Catalyst	Feedstocks	^{a}Conditions	Yield (%)	Ref.
1	Mo-Mn/γ-Al_2O_3-15 % MgO	WCO	27:1, 3, 100, 240	91.4	[424]
2	Cu/Zn(10:90)/γ-Al_2O_3-800 °C	WCO	18:1, 6, 65±5, 180	88.82	[425]
3	Mg/MCM-41	WCO	8:1, 10, 80, 180	94	[426]
4	γ-Al_2O_3-CeO_2	WCO	30:1, 7, 110, 270	81.1	[427]
5	KAcZX	WCO	48:1, 6, 120, 180	80.8	[428]
6	Sr/ZrO_2	WCO	29:1, 2.7, 115.5, 169	79.7	[429]
7	Bi_2O_3-La_2O_3	JCO	15:1, 2, 150, 240	94	[430]
8	CaO-La_2O_3	JCO	25:1, 3, 160, 180	98.76	[431]
9	Mn@MgO-ZrO_2	Kernel oil	15:1, 3, 90, 240	96.4	[432]
10	HPA@ZIF-8	Rapeseed oil	10:1, 4, 240, 300	98.02^b	[433]
11	AWS/SO_4^{2-}	PFAD	15:1, 5, 80, 180	98	[435]
12	$[Zn(4,4'\text{-bipy})(OAc)_2]_n$	Soybean oil	3.2/5 (v/v), 2, 180, 120	98	[436]
13	K/TiO_2	Canola oil	36:1, 6, 70, 180	100^b	[437]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).

^{b}Conversion

8.4. Enzyme catalyst

In recent years, enzyme catalysts are widely examined for the production of biodiesel as they produce high-quality biodiesel, improve the product separation process, mild reaction conditions and most importantly their ecological benignness [438],[439]. Besides they do not form soap with FFA contrary to the alkaline catalyst and hence can be utilized in the biodiesel production in industrial scale. However, the high cost of the free lipase catalyst along with the limited long-term use has led to the exploitation of immobilized lipase catalyst to reduce the cost of the catalyst and its reusability. Apart from that, immobilized lipase catalyst showed greater tolerance to pH variation, high thermal stability and high substrate selectivity[440],[441]. To date, large number of literature are available in the field of biodiesel production using both free [442],[443],[444] and immobilized [445],[446],[447],[448] enzyme catalyst. It is reported that enzymatic transesterification reaction to produce biodiesel is the slowest pathway among all the known transformations. Taking into account, application of ultrasonic in the enzyme-catalyzed transesterification improves the reaction rate and hence reduces the reaction time[440],[449]. Thus, it can be a promising technique for the industrial-scale production of biodiesel in a very short time.

Table 22: Different enzyme catalysts reported for the production of biodiesel.

Sl. No	Catalyst	Feedstock	^{a}Conditions	Yield	Ref.
1	Lipase	WCO	3:1, 1.5, 65, 240	88	[442]
2	Thermomysis Lanugonosus Lipase	Rubber seed oil	4:1, 5, NR, 65	92.83	[443]
3	CalleraTM Trans L lipase	Soybean oil	4.51:1, 1.45, 35, 1440	96.9	[444]
4	Lipase@AC	Sardine oil	9:1, 10, 30, 600	94.5	[445]
5	Lipase@APTES-Fe_3O_4	*Aspergillus* lipid	4:1, 300^b, 45, 240	84	[446]
6	Lipase@ZIF-67	Soybean oil	6:1, 10, 45, 3600	78	[447]
7	Lipase@[bmim][PF_6]	Food compost	6:1, 40, 50, 840	72	[448]
8	Lipase@[bmim][NTf_2]	Food compost	6:1, 40, 50, 840	48	[448]
9	Lipase@Immobead	Blended non-edible oils	7.64:1, 3.55, 36, 120	94	[449]

^{a}Methanol-to-oil molar ratio, catalyst loading (wt. %), temperature (^{o}C), reaction time (min).NR: Not reported.

^{b}miligram

9. Future prospect

It is believed that several newly introduced catalysts will take a central position in the near future and help to produce biodiesel through eco-friendly and economically viable processes. The development of novel heterogeneous catalysis having both acid and basic sites on its surface will have promising future in biodiesel production technologies because they have ability to overcome the issues usually caused because of the utilization of homogeneous catalysts. The application of bifunctional solids can be a novel way in heterogeneous catalysts mediated biodiesel production, because they showed the capability to accomplish simultaneous esterification and transesterification reactions in one-pot. In addition, the development and application of nanocatalysts will be a milestone in biodiesel production. These nanocatalysts will be the next generation catalysts which will help to develop most effective, sensitive, sustainable and economically viable technology for the FAME production in the near future. Although recent advances in the developments various homogeneous, heterogeneous and nanocatalyst showed promising future for biodiesel industries or biorefineries, more efforts are required to develop even more effective and cheap catalysts which will help to overcome the present issues all the above-mentioned catalysts and increase the efficiency of biodiesel production sustainably.

10. Conclusion

The exponential growth in the human population around the globe and industrial globalization tremendously increases the demand for petroleum fuels like diesel for various purposes. However, considering the limited resources of fossil fuels, searching for a novel, renewable and sustainable alternative fuel was required. In this context, researchers focused on FAME production from different renewable sources as an effective way. A variety of methods have been proposed for biodiesel production however, among all these existing methods transesterification is considered as the foremost choice.

Transesterification reaction involves the use of a particular catalyst and it is usually based on catalytic systems. Two kinds of catalyst i.e. homogeneous and heterogeneous catalysts have been usually utilized for transesterification reaction. The use of homogeneous catalysts is found to be promising as far as biodiesel production is concerned but it is associated with certain limitations. The homogeneous catalysts based transesterification reaction involves the consumption of high energy, moreover, the treatment of wastewater generated is essential due to the presence of unreacted chemicals. These limitations created the need for the development of efficient catalysts which was completed in terms of heterogeneous catalysts. These catalysts attracted a great of attention from the scientific community all over the world because of its several advantages over homogeneous catalysts such as the simple realization of continuous reactors, production of cleaner glycerol, and the absence of both the alkaline catalyst neutralization step and the necessity to replace the consumed catalyst. Due to these advantages, heterogeneous catalysts have opened up the chance for another powerful pathway for FAME production. However, the reactivity of the solid catalyst is dependent on several variables which mainly involve the oil type, alcohol to oil molar ratio, temperature, type of reactor, etc. therefore, selection of these variables at an optimum level is a crucial step. The heterogeneous catalysts are considered comparatively promising because only external-surface active species of porous solid support involved in the reaction and these catalysts can be recovered in some cases. However, in case of certain catalysts like CaO, leaching was reported which adversely influences the reaction and hence, researchers are looking at nanotechnology as new hope.

Nanotechnology is the most emerging branch of science having promising applications in catalysis. Moreover, it reported to have the ability to fabricate the catalyst surface in order to meet the prerequisites of explicit applications and beat the different issues related to both homogeneous and heterogeneous catalysts. Nanocatalysts can act as an interface between homogeneous and heterogeneous catalysts having the possibility to develop promising solid-acid or solid-base catalysts which can be easily recovered using conventional filtration and centrifugation techniques. The development and use of magnetic nanoparticle-supported catalysts is a path-breaking research because such catalysts can be easily recovered by using a simple magnetic field and reused for progressive reaction cycles which helps to reduce the overall process cost involved in biodiesel production which is the ultimate aim.

It is well proven that the application of biological catalyst (enzyme) is more effective over all kinds of chemical catalysts, but the involvement of expensive enzyme increases the overall cost of the FAME production process. In this context, immobilization of such enzymes on the surface of various magnetic nanoparticles was found to be a novel concept because of the easy recovery of the immobilized enzyme along with magnetic nanoparticles and its reusability. Moreover, it also solves the problem of leaching of the enzymes during the reaction due to immobilization. Although nanocatalysts reported to have promising applications, the toxicological concerns associated with nanoparticles is a topic of debate because there are mixed opinions from the scientific community.

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