General Concepts for Catalytic Synthesis of Biodiesel from Waste Cooking Oil

Yun Hin Taufiq-Yap and Nasar Mansir

Abstract The current global energy crisis is as a result of human population growth and technological advancements in developing countries. Beside the potential depletion of conventional fossil fuel reserves, fossil fuel is related with some environmental problems, i.e. global warming, high toxicity and non biodegradability, hence it is considered as non sustainable source of energy. Biofuels, particularly biodiesel is considered as one of the most promising and long-term energy source that can replace the fossil fuel. This is due to its biodegradability, non toxicity, safe and recyclable nature. Nevertheless, biodiesel production through the utilization of homogeneous catalytic system from food grade vegetable oil is no longer justifiable by industries in the near future, principally as a result of food versus fuel rivalry and other environmental issues associated to the conventional homogeneous catalytic system. Employing the waste cooking oil as feedstock to produce biodiesel using heterogeneous solid catalyst would help in making biodiesel fuel affordable and sustainable. This chapter review the general concepts of catalytic synthesis of biodiesel from waste cooking oil using heterogeneous catalysts and the problems associated with conventional catalysts usage for biodiesel production. The chapter also discussed the biodiesel quality assessment parameters.

Keywords Fossil fuel · Biodiesel · Waste cooking oil · Homogeneous catalyst
Heterogeneous catalyst · Biodiesel properties

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1 Introduction

Energy is generally considered as the backbone of modern scientific and technological advancements and therefore need to be harnessed in a sustainable way. Even though conventional fossil fuel will maintain to remain relevant as a major source of energy in the near future, but the oil reserves are imminently declining globally [1–5]. Besides, conventional fossil fuel is associated to some environmental and health problems such as Green house gases (GHGs), global warming, non biodegradability and poisonous exhaust from automobile [6]. The aforementioned problems triggered the search for renewable source of energy alternative to traditional fossil fuel. The recent discovery of biofuels would provide lasting solution to the problems of conventional fossil fuels. Biofuels are considered as alternative replacement to fossil fuels due to their less toxic emissions of carbon dioxide (CO_2), free sulphur content, biodegradability and feedstock availability [7, 8].

Biodiesel was found to be promising alternative considering its similarities in chemical properties with petroleum based diesel such as high flash point, pour point and improved cetane number [9, 10]. Study showed that Biodiesel demand is estimated to doubled or tripled by the year 2020 and beyond due to increase in population growth in developing countries and technological advancements [11, 12].

Commercialization of biodiesel production to outmatch the popular conventional fuel is the only way to solve the current and future energy challenges. Nevertheless, biodiesel production at industrial scale remains the major issue considering the nature of the feedstock and catalytic system used [1]. Employing low grade feedstock like palm fatty acid distillate (PFAD), *Jatropha curcas* oil and waste cooking oil for commercial production of biodiesel would help in reducing the high production cost of biodiesel due to its easy accessibility and low cost [13–15]. Nevertheless, the conventional catalytic system (homogeneous catalyst) could not work on these feedstock as they contain some impurities such as moisture and high FFA content [2, 16, 17]. Homogeneous liquid catalysts like Potassium hydroxide (KOH), Sodium hydroxide (NaOH), alkoxide and Tetraoxosulphate (VI) acid (H_2SO_4), can only be employed for biodiesel from high grade vegetable oils like palm oil, soybean oil and sunflower oil [18]. Nevertheless, the high cost of fresh vegetable oils, which account for more than 80% of total production cost of biodiesel, therefore, will make biodiesel production very expensive [11, 19, 20].

Separation and purification steps of biodiesel from the post reaction mixture would also make biodiesel very difficult as it requires considerable amount of energy and large amount of water during washing, hence polluting the environment by the generated waste water [21–23].

To overcome such issues, heterogeneous catalytic system is now considered as effective route for biodiesel production from low grade feedstock with least marked difficulty [24–26]. Moreover, heterogeneous catalysts can be recovered and reused several times before complete loss of activity, hence demonstrating more economical viability for commercial production of biodiesel [27, 28].

2 Feedstock for Biodiesel Production

Commercialization of biodiesel production is solely depends on the feedstock. The feedstock of biodiesel production can be categorised into three different categories. These include first generation, second generation and third generation feedstock.

2.1 *The First Generation Feedstocks for Biodiesel*

The first generation feedstocks are mainly consumable oils that are used as a source of food. This category contains mainly vegetable oils of high purity containing less than 1% free fatty acid. Example of these oils include palm oil, sunflower oil and soybean oil, were initially the most used feedstock for biodiesel synthesis [29]. The palm oil is commonly employed as feedstock for biodiesel production in Asia, particularly Malaysia and Indonesia. This is due to the abundant production of palm oil in the area. Malaysia is ranked as the second leading palm oil producer in the world [30]. Hence, in the advent of biodiesel, palm oil was used popularly as feedstock.

However, the continual usage of these feedstocks for biodiesel production will not be sustainable considering its high cost, and possible food/fuel competition which may pose great danger of hunger and starvation in the developing world. Moreover, the utilization of the available arable lands for the production of such feedstock may results to deforestation and damage to the ecosystem and consequently the ecological imbalance. Besides, the food grade oils are only fit to homogeneous liquid catalysts. However, these catalysts are difficult to separate after use and can pollute environment through water washing [2]. The aforementioned, are the major drawbacks for the utilization of edible oils for the commercialization of biodiesel [31–33].

2.2 *Second Generation Feedstocks for Biodiesel*

The second generation feedstocks are mainly the non-edible feedstocks [34]. These feedstocks are not suitable for human consumption as a result of toxic compositions present in the oils hence are considered as promising and sustainable [35]. Besides, the non-edible oils can successfully surmount the issue of potential food versus fuel competition. Moreover, non edible oil bearing crops can be cultivated on the unproductive/infertile land unfavourable for food crops cultivation. The non edible crops can grow along the roads, rail ways, follow lands and degraded forests [34]. Therefore, planting non edible crops can help in mitigating poverty in the rural areas at the same time contributing great impact for the sustainability of biodiesel production. The common examples of such feedstocks are *Jatropha curcas* oil, *Moringa oleifera* oil, *Mahua* oil, *Tobacco* oil, Karanja oil, Linseed oil etc. [29]. Waste cooking oil or used oil, PFAD, Yellow grease and animal fats are also considered as sustainable and promising second generation feedstocks for biodiesel production [36, 37].

2.3 Microalgae Oil

Microalgae oil is also non edible oil and considered as the third generation feedstock. Microalgae are the most promising, economically viable and inexhaustible feedstocks for the production of biodiesel when compared to second generation feedstock [38]. High oil content microalgae can potentially produce oil yield 25 times much higher when compared to that of conventional biodiesel bearing crops like palm oil, sunflower oil etc. Microalgae with an average oil production of at least 70% by weight of dry biomass needed only 0.1 m^2 year per kilogram biodiesel of land to produce 121,104 kg of biodiesel per year [39]. The above mentioned large production value of this plant made it to be recognized as excellent source of biodiesel feedstock [35]. Moreover, microalgae reproduce themselves and completing an entire life cycle within few days. Microalgae does not require fertilizer or even fresh water, as it can survive in salt or even contaminated sea or pond water. Herbicides and pesticides are not in the range of its requirement for cultivation. Beside the huge oil content, bio-compensation of CO_2 emissions is another added advantage of this plant.

Studies showed that, only 1 kg of dry algal biomass absorbs about 1.83 kg of CO_2 and therefore improving the air quality [39–44]. Nevertheless, despite the striking advantages of microalgae as a source of feedstock for biodiesel production, serious technological problems related to microalgae oil production should be addressed before they become credible contenders for biodiesel production in commercial scale [11].

3 Waste Cooking Oil as Viable and Sustainable Feedstock for Biodiesel Production

Generally, biofuels are meant to represent a potential source of renewable energy that could feasibly replace the conventional fossil fuels and provide eco-friendly fuel with less ecological problems (Global warming, Green house gas effects). Biodiesel is currently one of the most widely accepted alternative renewable sources of energy option to conventional fossil fuel. However, biodiesel production cost remains the major issue today. Current commercial production of biodiesel depends entirely on edible vegetable oil such as rapeseed (6.01 million ton), palm oil (6.34 million ton), Soybean oil (7.08 million ton) and some non-edible oil such as Castor oil and *Jatropha curcas* oil as major feedstocks worldwide [45, 46]. The use of conventional feedstocks (edible oils) for biodiesel accounts for more than 80% of total biodiesel

Table 1 Common fatty acid composition of plant based oil [55]

No.	Fatty acid	Formula	Structure	wt%
1.	Palmitic acid	$C_{16}H_{32}O_2$	16:0	7.3
2.	Stearic acid	$C_{18}H_{36}O_2$	18:0	4.0
3.	Oleic acid	$C_{18}H_{34}O_2$	18:1	26.9
4.	Linoleic acid	$C_{18}H_{32}O_2$	18:2	60.0
5.	Linolenic acid	$C_{18}H_{30}O_2$	18:3	0.5

production cost. Hence making biodiesel more expensive than the petroleum based diesel and therefore, not sustainable.

Moreover, continual usage of traditional edible oils as feedstock for biodiesel may result to future food versus fuel competition hence, violating one of the fundamental objective of biodiesel production [47]. *Jatropha curcas* oil is particularly remarkable feedstock for FAME production as it has about 40% oil content and can grow on infertile soil thereby, avoiding competition with arable land for food crops, however, *jatropha curcas* seeds are toxic in nature, hence the harvest requires severe labour [20]. Recent studies suggested that the production cost of biodiesel could be reduced to halve through the utilization of waste cooking oil in comparison to the high grade vegetable oils [20].

Currently, about 15 million tons of waste fried oil is annually been disposed into water bodies or land across the globe. Such large amount of low cost feedstock noteworthy special consideration, as it could bridge significant gap in current biodiesel demands [45]. Waste cooking oil when properly utilized can produce biodiesel with less CO_2 emission at relatively low cost and thereby making it economically and socially viable as a renewable fuel. Besides that, converting waste cooking oil into biodiesel could help significantly in reducing the environmental pollution caused by its disposal into water bodies and land [48].

Nevertheless, some chemical changes occur to waste cooking oil as a result of heating at high temperature during cooking/frying processes, which increases the level of FFA and some impurities like water content. Basically fresh vegetable oil contained triglyceride diglyceride, monoglyceride and FFA usually ($<1\%$) [49]. High FFA and water contents in the feedstock hampers biodiesel production due to subsequent soap formation when basic catalyst is used [8, 50, 51]. These challenges must be taken into consideration before using it as a feedstock [52].

Different feedstocks for biodiesel synthesis have different fatty acid content and in turn can influence the biodiesel yield. Other fuel properties like acid value, cloud point, cetane number, pour point, flash point, oxidation stability, cold filter and plugging point could also be influence by FFA composition of the feedstock [53, 54]. Basically, the vegetable based oils comprised of five major fatty acids components as presented in Table 1, namely; Palmitic (16:0), Stearic (18:0), Oleic (18:1), Linoleic (18:2) and Linolenic (18:3).

Waste cooking oil has so far been regarded as one of the cheapest feedstock for biodiesel synthesis, with dual advantage [50]. Utilizing it as feedstock for biodiesel is at the same time making the environment cleaner for not being disposed into the water bodies that could pollute the water. Hence waste cooking oil is considered as economically viable and environmentally benign feedstock for biodiesel production on a commercial scale.

4 General Overview and Role of Catalyst in Biodiesel Synthesis

A catalyst is defined as a substance or material, that when added in the balanced chemical reaction speeds up the chemical reaction by lowering its activation energy to reach the chemical equilibrium between the reactants and products without changing the thermodynamic equilibrium of the system [56]. It is usually added in a minute amount in comparison to the quantity of the reactants. Under normal circumstance, the catalysts could not be consumed during the reaction and therefore unchanged after the reaction process.

However, in some cases the catalyst inhibits the reaction by being consumed and regenerated, while in other cases it seems not to include in the process and functions by high calibre of surface characteristics [57]. In biodiesel synthesis reactions, catalysts are classified into homogeneous and heterogeneous.

A homogeneous catalyst is having similar phase with the reactants while the heterogeneous catalyst system has different phase with the reaction medium.

Heterogeneous solid catalysts are now considered as the most feasible with regard to biodiesel production reaction process. This is due to their low cost, reusability and easy separation from the post reaction mixture and disposal after the reaction. It is very important to characterize these materials and classify their function carefully in terms of selectivity and reactivity in chemical reactions. Activity and selectivity of the catalysts are important characteristics that could be measured by performing the chemical reaction [58].

4.1 Catalysis

Catalysis can be defined as a technique representing the vital technology for accelerating the essential chemical conversion, which is a key to recognize environmentally friendly and commercially feasible reactions for transforming energy carriers to direct usable energy. Catalysis could also be defined as a technique used to perform chemical conversions in the wisest use of materials and energy leading to the acceleration of chemical reactions by the addition of a catalyst. Moreover, the use of heterogeneous catalysts for chemical conversions is not only decreasing the total energy input needed for the production processes, but also improves two considerable catalyst aspects, i.e. selectivity and thermal stability, thus leading to ecologically benign green technology.

4.2 Industrial Application of a Catalyst

The catalyst was first employed for industrial application by J. Roebuck in 1746 in the process of manufacturing lead chamber sulfuric acid. The applications of catalyst in large proportion have been adopted by the chemical industry since then. Initially, only pure components were used as catalyst, however, from the year 1900 to date multi component catalysts were studied and now employed in different chemical industries [59, 60].

Moreover, in the last 40 years, more than three hundred solid acid and base catalyst have been developed for various functions in the food and chemical industries. The structures and surface properties of the newly developed catalysts are being elucidated by newly developed methods and highly sophisticated techniques. The characterized solid base and acid catalysts are usually applied in different chemical reactions. The roles of acid and base properties are being measured for catalytic activities during a chemical reaction.

The heterogeneous acid and base catalysts are now considered largely as ecologically and economically viable in the field of catalysis. This is due to their advantages over homogeneous acid and base catalysts. The advantages include easy separation after use, less corrosive, ecologically benign, less disposal problem and reusability for more than one reaction cycle. Additionally, solid catalysts could be designed to possessed high activity, selectivity and stability. Hence, the emergence of heterogeneous solid acid and base catalysts is considered as a breakthrough in chemical industries, as it has solved most of the problems associated to homogeneous liquid catalysts.

Industrially, the catalyst plays a fundamental role in the improvement of sustainable reactions, which have primarily allowed the present and future universal production and exploitation of energy and chemicals, at the same time mitigating the harmful consequences to the surroundings and has the significance to key technology. Presently, larger industrial operations employed the use of modern catalytic system for the production of energy and chemicals. These operations include transesterification/esterification reaction for biodiesel, catalytic cracking of biofuels and fossil fuels, synthesis of ammonia and methyl alcohol. Other industrial application of catalyst for energy and chemical synthesis are; alkylation, isomerisation, dehydration and condensation, amination, cracking, etherification aromatization, hydration, hydrocracking, oligomerization and Polymerization [61]. Catalyst application at industrial scale, which account for about 85–90% of the output of the chemical manufactured through catalytic routes generated about $900 billion in products worldwide [62].

4.3 Homogeneous Catalysts for Biodiesel Production and Their Problems

Production of biodiesel in commercial scale from vegetable oil relies solely on homogeneous catalyst system considering their major advantage of reduced effect of mass transfer resistance, hence faster reaction efficiency due to high acid and basic sites distribution when compared to the heterogeneous catalysts. The homogeneous catalysts used in the synthesis of biodiesel could either be acidic or basic in nature. Basic homogeneous catalysts are the most frequently used catalysts to support the biodiesel production process at industrial scale. This is due to the faster reaction efficiency of base-catalysed transesterification reaction process when compared to acid catalysts, which generally react at slower rate; consequently, producing high biodiesel yield at mild reaction conditions [63]. However, the FFA and water content of the feedstock are the fundamental consideration on choosing the type of catalyst to be used in a particular biodiesel production reaction.

The frequently employed homogeneous catalysts for biodiesel synthesis are hydroxides and alkoxides of alkali metals such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (CH_3ONa) and potassium methoxide (CH_3OK) [64, 65]. In all of the listed homogeneous catalysts, KOH and NaOH are the most frequently employed catalysts for biodiesel production at commercial scale mainly due to their capacity to assist transesterification reaction at relatively mild reaction conditions and high reaction rate, which moves 4000 times faster when compared to acid catalyst reaction rate [66]. Excellent biodiesel yield is believed to be achieved at short reaction time, and most importantly, these catalysts are cheap and easy to prepare [63]. Several studies have been conducted on different feedstocks to produce biodiesel using homogeneous catalysts. Uzun et al. [65] reported the biodiesel yield of 96% at a reaction temperature of 50 °C, and 30 min reaction time when NaOH catalyst was used on soybean oil using methanol as reaction medium. Similar studies was conducted by Fadhil and Ali [67], where KOH catalyst was used to transesterify Heckel fish oil, and 97% of biodiesel yield was recorded at 32 °C reaction temperature, 60 min reaction time, 6:1 methanol to oil ratio and 5.5 wt% catalyst loading. Nevertheless, formation of soap and other unwanted emulsions as a result of FFA content (>1%) and other impurities from low grade feedstock is another problem that may hinder commercialization of biodiesel [68].

The prominent homogeneous acid catalysts for methanolysis are mineral acids such as Hydrochloric acid (HCl) and Sulphuric acid (H_2SO_4) [69]. Others are nitric acid (HNO_3), aluminium chloride ($AlCl_3$), organic sulfonic acid and phosphoric acid (H_3PO_4) [63]. Homogeneous acid catalysts generally have a slow rate of reaction and therefore, take long time during reaction process to esterify feedstock to biodiesel. Marchetti and Errazu [70] reported the biodiesel yield of 96% from model oil prepared using oleic acid and sunflower oil when H_2SO_4 was used as a catalyst at 55 °C reaction temperature, 6.126:1 methanol to oil molar ratio, 2.26 wt% catalyst loading and 240 min was the time taken to satisfactorily completes the reaction process. In a related study, Soriano et al. [23] reported that 98% yield of biodiesel was achieved when canola oil was subjected to methanolysis using $AlCl_3$ as a catalyst under the reaction temperature of 110 °C, catalyst loading of 5 wt%, methanol to oil molar ratio of 1:1 and 1080 min as reaction time. However, homogeneous catalysts made biodiesel production difficult and expensive due to the peculiar problems associated to these catalysts. The major drawbacks to homogeneous catalysts that severely affect the biodiesel production at industrial scale include high cost of production as these catalysts fit only high purity feedstock such as palm oil, sunflower oil, soybean oil, etc.

Besides, separation of catalysts after the reaction process involves regular water washing that requires a substantial amount of water and energy, which will make biodiesel production difficult and expensive. Consequently, the waste water generated during the washing of the catalyst would pollute the environment and subsequently distort the ecosystem. Hence, homogeneous catalysts are not environmentally and economically benign for the sustainable biodiesel production at industrial scale.

4.4 Heterogeneous Catalysts for Biodiesel Synthesis

Heterogeneous catalysts are mainly solid catalysts that are in different phase with the reacting medium. Solid catalysts can easily be recovered and reused more than once in a chemical reaction. These catalysts could be acidic, basic or bifunctional.

4.4.1 Solid Acid Catalysts for Biodiesel Synthesis

Recently, heterogeneous solid acid catalysts are receiving greater attention from scientific and industrial point of view for biodiesel production. This is due to their several advantages over their homogeneous counterparts. Heterogeneous solid acid catalysts when properly utilized are expected to yield outstanding grade biodiesel from vegetable based oils. Moreover, unlike homogeneous acid catalysts, heterogeneous acid catalysts are not associated with corrosion of biodiesel production plant/equipment [71]. Solid acid catalysts promote esterification process of oleic acid or PFAD to synthesize methyl ester and water as the major products under low temperature [72].

More importantly, heterogeneous acid catalysts could simultaneously accelerate both transesterification of triglycerides (TGs) and esterification reactions of FFA. The two reactions; transesterification and esterification are catalysed by Bronsted acid species and Lewis acid species respectively [63, 73, 74]. It is generally assumed that catalytic biodiesel synthesis reaction process occur in the same way for both homogeneous and heterogeneous acid catalysts except that, the heterogeneous acid catalysed reaction is influenced by the catalysts surface, which depends greatly on the interconnected system of large pores, surface acid sites and hydrophobicity [63]. Heterogeneous acid catalysts can esterify waste oil like palm fatty acid distillate which has over 85% FFA content and other low grade feedstocks like waste cooking oil to biodiesel [8].

Nevertheless, heterogeneous acid catalysts can only perform transesterification reaction under severe reaction conditions such as high reaction temperature, low reaction rate and long reaction period [2]. These drawbacks may probably make biodiesel production difficult and expensive. Several studies were reported on biodiesel production from low grade feedstocks using heterogeneous solid acid catalysts under severe reaction conditions (Table 2). Hence, the new route of catalytic system that can perform biodiesel production process on low grade feedstock under moderate reaction conditions is needed.

4.4.2 Solid Base Catalyst for Biodiesel Synthesis

Solid base catalysts constitute of alkaline metals and alkaline earth metals which made the group one and two of the periodic table. These catalysts have been employed as catalysts for biodiesel production process. Heterogeneous base catalysts could be an alkaline earth metal in a single form, alkali metal in a supportive form, other mixed oxides of alkaline earth metal or hydrotalcites and anionic ion-exchange resins.

Alkaline earth metal oxides catalysts if properly modified could have the capacity to assist transesterification reaction of low grade feedstock such as waste fried oil in a single reaction stage route, due to the possession of excellent basic potency [84]. The basicity potency of group II metal oxides and other hydroxides is advanced with the increase in the atomic number ranging from magnesium (Mg) in period II to Barium (Ba) in period VI, which considerably affects their catalytic potential for transesterification of triglyceride [85].

The source of basic centres in alkaline earth metal oxides might be linked to the existence of $M^{2+}$and O^{2-} ion pair as well as surface hydroxyl group in a different coordination environment. The surface oxygen of these oxides may possibly be affected by the surface composition of the solid catalysts and calcination temperature. Moreover, the specific surface area, level of leaching of the active site of the catalyst in the reaction intermediate, basicity and selectivity during the biodiesel reaction process are deemed to be considered as important features in choosing the suitable catalyst for biodiesel production [63].

The most commonly used basic heterogeneous catalyst for transesterification process is calcium oxide (CaO) [86]. This is due to the possession of higher basicity, low solubility, easy to handle and most importantly availability of CaO at relatively low cost. Additionally, CaO derives its popularity for catalysis as a result of its abundance in different natural resources in the form of calcium carbonate ($CaCO_3$). Apart from lime stone which is natural but non-renewable source of $CaCO_3$, other renewable natural sources are egg shells [87, 88], crab shells [87], capiz shells [89], snail shells [90], mussel shells [91] and oyster shells [92] among others. Proper employment of these shells for the synthesis of CaO will considerably reduce the over dependency on non-renewable lime stone as a source of CaO. Waste egg shell is believed to have a high content of $CaCO_3$ having a composition of about 97.1%. This shell when thermally treated at 900 °C for 2 h would result in the synthesis of CaO catalyst [63].

Table 2 Literature reports of solid acid catalyzed biodiesel production at high reaction conditions

Catalyst	Preparation method	Reaction conditions				Feedstocks	Yield (%)	Refs.
		Temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Methanol to oil molar ratio			
$Al_2O_3/TiO_2/ZnO$	Co-mixing	200	6	8	1:1	Colza oil	93.7	[5]
Ar-SBA-15	Not reported	260	2.5	1	20:1	Crude palm oil	90	[75]
$Al_2O_3/ZrO_2/WO_3$	Co-precipitation	175	1	4 g	40:1	Soybean	100	[76]
$Al_2O_3/TiO_2/ZnO$	Sol-gel	200	8	5	Not specified	Colza oil	93.7	[77]
$Al_2O_3/ZrO_2/WO_3$	Wet impregnation	200	20	4 g	4.5:1	Soybean oil	>90	[78]
Ar-SBA-15	Direct mixing	140	6	2	20:1	Crude palm oil	90	[75]
CsHPW	Precipitation	200	10	3	20:1	Oleic acid-Soybean mixture	90.4	[79]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	Precipitation	260	1	3	40:1	Sesame oil	92	[80]
Carbonized and Sulfated asphalt	Carbonization	260	1	2.5	18.2:1	Waste cooking oil	89.9	[1]
$Mn_{3.5x}Zr_{0.5y}Al_xO_3$	Co-precipitation	150	5	2.5	14:1	WCO	>93	[81]
SO_4^{2-}/TiO_2-SiO_2	Impregnation	200	3	4	9:1	Used cooking oil	90	[6]
$TiO2/SO_4^{2-}$	Precipitation	230	2	8	12:1	Coconut oil Cotton oil	86.3 90	[75]
VOPO4.2H20	Not reported	150	1	2	1:1	Used cooking oil	80%	[82]
ZrO_2/SO_4^{2-}	Sulfonation	200	1	1	6:1	Palm kernel	90.3	[83]

Besides the cost-effective benefits, the capacity of CaO as a solid catalyst for biodiesel synthesis can match the conventional homogeneous catalysts having achieved outstanding conversion yield over some selected feedstocks. Kawashima et al. [93] reported 90% biodiesel yield when transesterification reaction was performed on rapeseed oil using CaO as catalyst and methanol as reaction medium, other reaction conditions used are 60 °C as reaction temperature, 0.1 g catalyst weight and 3 h reaction time. Similarly, Lee et al. [94] reported biodiesel yield of 86.75% using palm oil and obtuse horn derived CaO as feedstock and catalyst under the optimum reaction parameters of 5 wt% amount of catalyst, 6 h reaction time and 12:1 methanol to oil ratio. CaO material irrespective of its source, is unstable, hence, prone to poisoning effects when exposed to atmospheric medium i.e. carbon dioxide (CO_2) and moisture (H_2O), which would results in the formation of calcium carbonate ($CaCO_3$) and calcium hydroxide $Ca(OH)_2$ layers, respectively on the catalytic surface [95]. These effects distort and block the catalytic active sites hence lowering the activity of the catalysts and biodiesel yield [63].

Despite the encouraging results obtained using these catalysts, CaO catalyst alone could not transesterify impure oil such as waste fried oil and *Jatropha oil*. This is due to the existence of high FFA (>3%) composition and other impurities such as water in a single run process. In order to transesterify low grade feedstock like waste cooking oil using CaO catalyst, two stage process must be involved to reduce the FFA content to (<1%) [96]. These processes are considered as time and resource consuming, making biodiesel production difficult and expensive. Hence, for the CaO catalyst to work on low grade feedstock like waste cooking oil and Jatropha oil containing high FFA (>3%), there is need for further modification that will provide some acid centres so that to esterify the high FFA present in the feedstock for efficient and sustainable biodiesel production. The modification of basic heterogeneous catalysts like CaO for high activity on low grade oil could be doping with other metal oxides from transition group. Some transition metal oxides like MoO_3, WO_3, TiO_2 or ZrO_3 possessed some acidic properties that would enhance the catalytic activity during transesterification of low grade feedstock like waste cooking oil.

4.4.3 Bifunctional Solid Catalysts

Generally, separation and waste water disposal problems, corrosion of biodiesel refining equipments associated to homogeneous catalysts, increases concerned over the adoption of heterogeneous catalysts for biodiesel synthesis [2, 27]. Utilization of solid catalysts for biodiesel synthesis can overcome the separation problems. Solid base catalysts in which basic component comes from waste material like egg shell is considered as environmentally benign due to its biodegradable property hence can greatly reduce the environmental problems. Over the last few years, there were greater concerns over the heterogeneous catalysts whereby intensive studies were conducted for transesterification reactions over these catalysts, [49, 94, 97–99].

The best heterogeneous catalysts should have strong basic sites, large surface area, large pores, less toxicity, high stability, less corrosive effect, ease separation, high reusability, less leaching effect and low cost of preparation [8].

Mixed oxides catalysts are originated from metal oxides particularly alkali earth metal oxides, lanthanide metal oxides or other transition metal oxides. Mixed oxides catalysts could be basic, acidic or bi-functional (having both acidic and basic properties). Bi-functional heterogeneous catalyst if utilized properly could perform transesterification and esterification of TGs and FFA simultaneously under moderate reaction conditions, respectively. This is because; the bi-functional catalysts are having both basic and acidic sites and therefore can perform simultaneously esterification and transesterification reaction during biodiesel synthesis. Additionally, bi-functional catalysts can be modified to bring in the needed physicochemical properties that could easily overcome the problem of high FFA and moisture content present in the impure feedstock like waste cooking oil during the transesterification reaction [25]. Hence, bifunctional heterogeneous catalysts could become excellent option catalysts to overcome the associated problems with other catalysts. Over the recent years, several researches were undertaken using modified mixed oxide catalysts with bifunctional activity to produce biodiesel from high FFA feedstock under mild reaction conditions as presented in Table 3.

5 Biodiesel Synthesis and the Reaction Mechanisms

Fatty acid methyl ester (FAME) or conventionally biodiesel is generally synthesized by the transesterification reaction of triglycerides (TGs) or esterification of FFA. During transesterification reaction, 1 mol of triglycerides react with 3 mol of methanol, catalyst and temperature over a period of time to generate 3 mol of methyl ester (biodiesel) and glycerol as presented in Fig. 1. Chan and Fang [102, 103] reported the formation of transesterification reaction in the 3 step processes as depicted in Fig. 2. Transesterification reaction is reversible reaction process and therefore needs high amount of methanol in order to move the reaction forward [63]. The excess methanol and glycerol produced together with FAME at the end of the reaction could be separated using centrifuge [1]. Catalytic conversion of triglycerides using solid base catalyst is much faster than esterification reaction using solid acid catalyst. This is due to the slower catalytic activity of solid acid catalyst resulting from lesser level of catalyst contact with reaction mixture [102].

In esterification reaction, 1 mol of FFA reacts with 1 mol of methanol in the presence of an acid catalyst to form 1 mol of FAME and water as shown in Fig. 3. Chen and Fang [102] reported the lengthy reaction rate of the esterification reaction process as a result of lesser catalytic activity when compared to base catalysed transesterification reaction.

Table 3 Literature report on biodiesel production from low grade feedstock using bifunctional catalysts

Catalyst	Preparation method	Reaction conditions				Feedstocks	Yield (%)	Refs.
		Temperature (°C)	Reaction time (h)	Catalyst loading (wt%)	Methanol to oil molar ratio			
Bi_2O_3–La_2O_3	Impregnation	150	4	2	15:1	Jatropha curas oil	93	[7]
CaO/La_2O_3	Co-precipitation	65	6	4	24:1	Jatropha curas oil	86.51	[100]
CaO-ZrO_2	Impregnation	65	2	10	30:1	Waste cooking oil	92.1	[82]
Cs-Zr/Al_2O_3	Impregnation	65	3	3	20:1	Waste cooking oil	90	[101]
Mo-Mn/γ-Al_2O_3-15wt% MgO	Wet impregnation method	100	4	4 g	27:1	Waste cooking oil	91.4	[25]
SO_4^{2-}/SnO_2-SiO_2	Impregnation	150	3	4	15:1	Waste cooking oil	>92.3	[21]

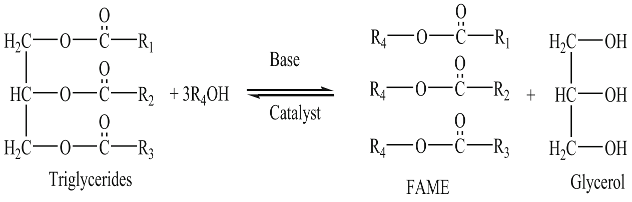


Fig. 1 General equation for transesterification reaction of biodiesel synthesis from triglycerides [63]

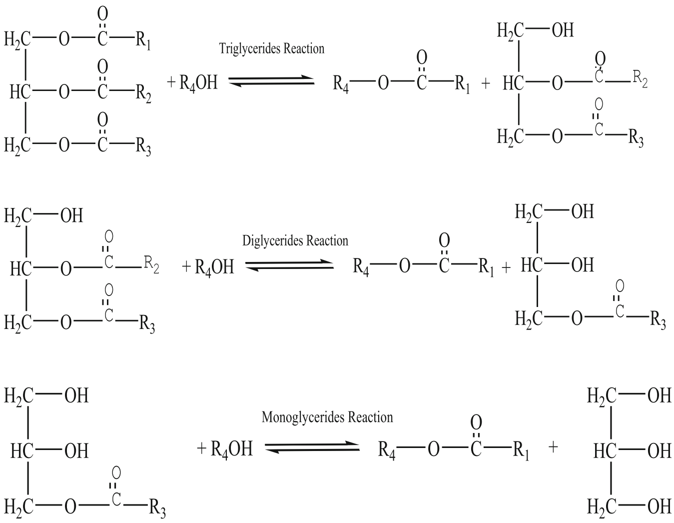
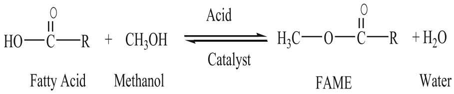


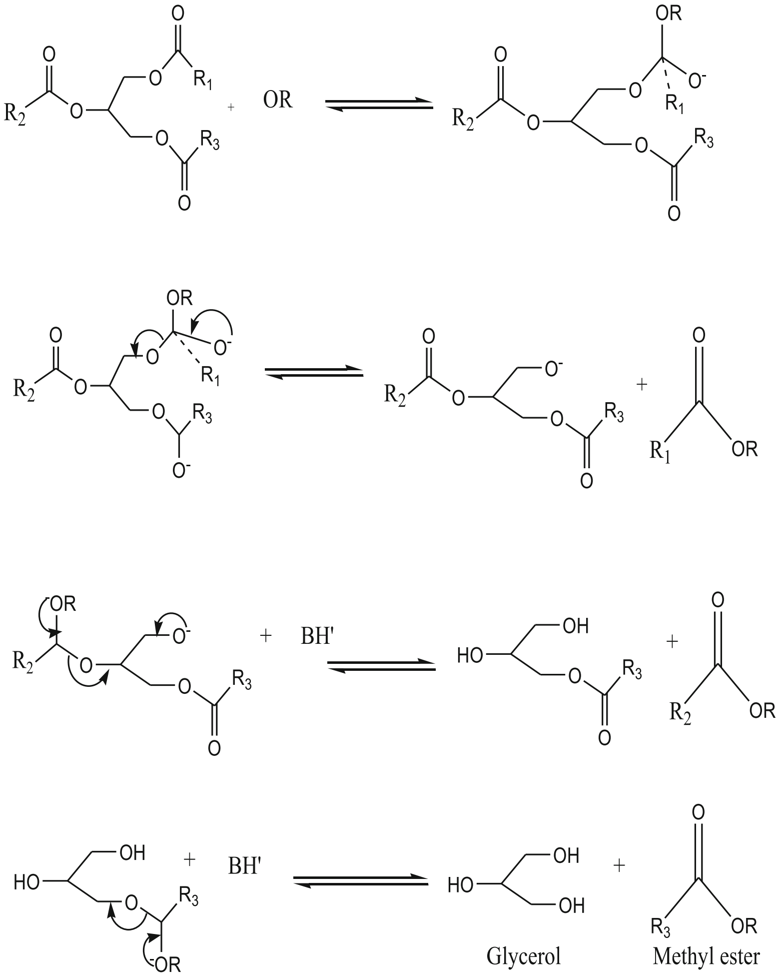
Fig. 2 Three step equations for transesterification reaction process of biodiesel production from triglycerides [63]

Fig. 3 Esterification reaction of biodiesel production from fatty acid



5.1 Mechanisms for the Transesterification Reaction Using Base Catalyst

The mechanisms for the transesterification and esterification reaction processes of heterogeneous catalysts and homogeneous catalysts are similar. The transesterification reaction of triglycerides (TG) to FAME and glycerol using base catalysts involves the formation of methoxide ion by dissociation of metal hydroxide (KOH) or metal oxide (CaO) into the methanol and encapsulated into TG- Methoxide microemulsion, then followed by nucleophillic attack of CH_3O^- on the carbonyl group on TG, which leads to the formation of tetrahedral intermediates. The second step is the



R_1, R_2, R_3 : Carbon chain of the fatty acids. R: alkyl group of methanol; OR: CH_3O^-; B: KOH: BH^+: $[K(OK)H]^+$

Fig. 4 Mechanism of transesterification for FAME production

intermediate break down to form methyl ester and diglycerides. The CH_3O^- active species are regenerated in the third step. The steps are repeated twice to produce monoglycerides, methyl ester and glycerol methyl ester, respectively as shown in Fig. 4.

5.2 Mechanism of Esterification Reactions Using Acid Catalyst

The mechanism for the esterification reaction of fatty acid using acid catalysts is depicted using ethanoic acid as a feedstock and sulfuric acid as catalyst in five steps reaction as presented in Fig. 5. In order to make the reaction mechanism simple and less confusing, all the mechanisms steps are shown in one way reaction.

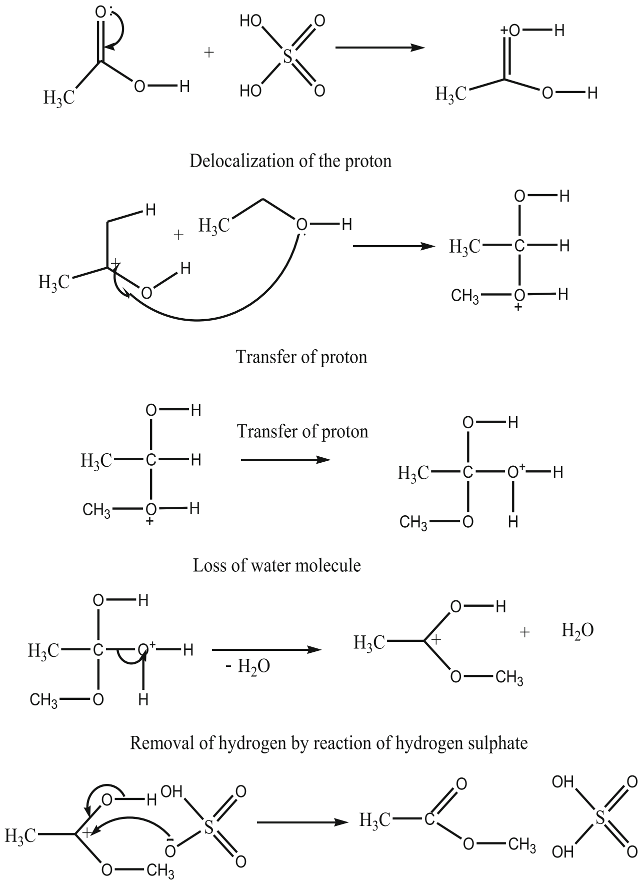


Fig. 5 Mechanism of esterification reaction for FAME production

6 Influence of Reaction Conditions for Biodiesel Synthesis

FAME is synthesized by either transesterification reaction process of triglycerides (major component of vegetable oil) or esterification reaction of lipid using basic or acid catalyst under certain reaction conditions. Biodiesel yield is mainly depended on the catalytic performance of the catalyst employed for the reaction. Moreover, the catalytic performance for the transesterification of triglycerides to FAME is influenced by five major factors, namely; temperature, amount of catalyst used, methanol to oil molar ratio, temperature of the reaction and time.

6.1 Methanol to Oil Molar Ratio

Methanol to oil molar ratio is one of the four main reaction conditions for the biodiesel reaction synthesis. This parameter plays an important role both in transesterification and esterification reaction process. During esterification of high FFA oil to biodiesel, which is also reversible, excess methanol is necessary in order to boost the reaction rate and biodiesel yield [4]. Conversions of triglycerides (TGs) to FAME occur when the reaction occur between the TGs molecules and the catalyst active site. At a molecular stage, TGs undergoes protonation at the carbonyl group to form the carbonation ion, which can also undergo a reaction to results in the formation of methyl esters [8]. Nevertheless, the catalyst active sites are submerged with excess methanol, which hampers the protonated TGs. Yan Li et al. (2010) reported that 90% of biodiesel yield was attained at the maximum of 18:1 methanol to oil ratio. No major increase in biodiesel yield was observed from 15:1 to 18:1 methanol to oil ratio hence 15:1 was adopted in view of economics and methanol recovery after the reaction [77]. The high amount of methanol during methanolysis was reported to be problematic during the separation process. This is due to the formation of emulsion from methyl ester and glycerol layers formed. The polar nature of the methanol made it to behave as emulsifier, which improves the formation of emulsion [4]. However, it is generally concluded that excess methanol increases the production yield and also enhances the interaction between TGs molecules and catalyst [14, 104].

6.2 Catalyst Loading

Catalysts are predominantly used during the catalytic conversion of triglycerides to biodiesel through the lowering of the activation energy and therefore, make the reaction faster. During the methanolysis of TGs or lipids, the amount of catalyst used in the reaction determines the overall yield of the produced biodiesel. The amount of catalyst used for a particular reaction is optimized to find the best loading for better biodiesel yield. Low amount of catalyst is employed in early reaction stages and the FAME yield is measured. The amount of catalyst would be increased in the subsequent reactions keeping other reaction parameters constant until the best FAME yield is recorded. Increase in amount of catalyst to 3 wt% during the transesterification reaction at 3 h reaction time was reported to enhance the overall FAME yield recording 90%. Subsequent increase of the loading to 4 wt% resulted to decrease in FAME yield to 83% [101]. Solubility of methanol was reported to be observed in high FFA content and other impure feedstocks like waste fried oil when low catalyst loading is used during methanolysis. Using high dosage of catalyst beyond the optimum loading during biodiesel synthesis results in declining of FAME yield through product absorption [105].

6.3 Reaction of Temperature

The transesterification reaction of triglycerides to FAME involves the use of reaction temperature, which provides the needed activation energy for the reaction to occur. During the transesterification reaction for biodiesel synthesis from vegetable based oil, increase in the reaction temperature helps the reaction to reach thermodynamic equilibrium and subsequently the rate of reaction, which facilitate the conversion of triglycerides to methyl ester. Moreover, insufficient reaction temperature during the transesterification reaction leads to incomplete conversion of triglycerides to biodiesel. Some studies reported that temperatures beyond optimal reaction temperatures lead to the formation of emulsions and therefore, diminishes the overall FAME yield conversion [7].

6.4 Reaction Time

In the catalytic conversion of triglycerides to biodiesel, time is considered as one of the fundamental parameters necessary for the reaction to occur, depending on the activity of the catalyst. Effect of reaction time is usually examined under the time range of 1–5 h, keeping other reaction conditions constant. Increase in reaction time enhances the conversion to triglycerides to FAME. Amani et al. [101] reported the considerable increase in FAME yield when reaction time was prolonged. According to their studies, the methyl ester yield was increased from 74% at 1 h to 90% at 3 h and 20:1 methanol to oil molar ratio. This phenomenon is attributed to slow mass transfer exhibited by heterogeneous catalyst reaction. Transesterification is reversible reaction and prolonging it beyond optimal reaction time may lead to moving the direction of the equilibrium backward and hence decrease the yield conversion.

Table 4 Diesel and biodiesel standard properties values in accordance with American Society for Testing and Materials (ASTM) [106]

Property	Diesel	Biodiesel
Standard	ASTMD975	ASTMD6751
Kinematic viscosity (mm^2/s)	1.9–4.1	1.9–6.0
Fuel composition	Hydrocarbon (C10–C21)	FAME (C12–C22)
Cetane number	40–55	48–60
Pour point (°C)	−35 to −15	−15 to 16
Cloud point (°C)	−15 to 5	−15 to 16
Flash point (°C)	60–80	100–170
Acid value (%)		
Water content (vol. %)	0.05	0.05
Density (g/cm^3)	0.85	0.88
Carbon (wt%)	87	77
Hydrogen content (wt%)	13	12
Oxygen content (wt%)	0	11

7 Biodiesel Quality Evaluation

The synthesized biodiesel can only be ascertained when it fulfils the standard fuel properties according to the accepted biodiesel fuel standard of American Society for Testing Materials (ASTM D751) and European standard (EN 14214). Table 4 presented the comparative summary of standard fuel properties between biodiesel and petroleum based diesel.

7.1 Kinematic Viscosity

Kinematic viscosity is one of the biodiesel fuel properties that are evaluated in the laboratory and ensure it falls within the accepted limit of biodiesel property standard before used in an internal combustion engines. Lower viscosity defined excellent kinematic viscosity of any synthesized biodiesel as it provides prevention against engine deposition. The kinematic viscosity of biodiesel is evaluated at a temperature of 40 °C based on ASTM and EN international standards. The accepted range of kinematic viscosity of biodiesel is 1.9–6.0 $mm^2\ s^{-1}$ as specified by ASTM D6751 and EN14214 biodiesel standards.

7.2 Pour Point

Pour point is considered to be one of the key cold flow properties of biodiesel fuel. It is defined as the lowest temperature at which the fluid/liquid stops flowing at lower temperature. Pour point is evaluated in the laboratory using cloud and pour point apparatus. The biodiesel sample is subjected to heating at a temperature of 45 °C in water bath and left to cool until the biodiesel sample reach down to ambient temperature (25 °C). Thereafter, the sample is introduced into the cloud and pour point equipment set at 0 °C. The analysis is performed by the subsequent decrease of the apparatus temperature to sub zero degrees and periodic check of biodiesel flow until the sample is no longer flows. The temperature at which the sample stops flow is then recorded as the pour point of the biodiesel sample. The standard pour point of biodiesel is specified to be in the range of -15 to 9 according to ASTM D6751.

7.3 Flash Point

Flammability is fundamental feature of any fuel particularly biodiesel. The flammability of biodiesel is referred as flash point (FP), which is define as the temperature required for a fuel to vaporises and sufficiently ignite and forms a flammable mixture with oxygen in controlled condition. The FP of biodiesel is evaluated based on ASTMD6751 and EN14214 standards, which is specified at the range of 100–170 °C.

7.4 Other Fuel Properties

Besides pour point, flash point and viscosity, acid value (mg/KOH), moisture content and (wt%) density (kg/m^3) are also fundamental in evaluating fuel properties of the synthesized biodiesel. The standard values of these properties must be in accordance to ASTM D6751 and EN14214 biodiesel standard specifications as depicted in Table 4.

8 Setbacks and Future Stance for Biodiesel Production

Taking into consideration of the current global energy challenges, there is need to urgently diversify into other possible sources of energy. The over dependent fossil fuel is no longer sustainable due to its un-renewable nature and environmental problems such as global warming. Renewable sources of energy like biofuels are considered as the best option to conventional fuel due to its biodegradability, less toxic and similar performance to fossil fuel.

Commercialization of FAME production to meet the global energy demand is the only solution to the current energy challenges. However, current FAME production is not sustainable considering the high production cost when high grade oil is employed as a feedstock and the conventional catalytic system, which is associated with separation and waste water generation problems. These problems could only be solved through the utilization of heterogeneous catalysts and low cost feedstock such as jatropha curas oil, PFAD and waste fried oil.

The conventional feedstock for FAME production is high grade oil with low FFA (<1%) content which can easily be converted to biodiesel at low reaction conditions. However, about 80% of total production cost of FAME will go to feedstock when high grade oil is used as a feedstock. Using Waste cooking oil as feedstock for FAME production will reduce the production cost to halve when compared to high grade vegetable oil as feedstock.

The heterogeneous solid catalyst could serve as the best option to homogeneous catalyst for the commercial FAME production considering the easy separation of the catalyst after the reaction process; more environmentally benign and more economical as it could be used more than once before it become inactive.

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