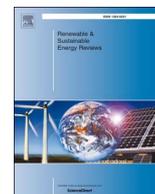




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## Modified waste egg shell derived bifunctional catalyst for biodiesel production from high FFA waste cooking oil. A review

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### ABSTRACT

Global energy crisis are as a result of gradual depletion of fossil fuel reserves, coupled with population growth in developing countries. Besides, fossil fuels are not environmentally benign as they are associated with problems, i.e. global warming, high toxicity and non biodegradability, hence it is considered as non sustainable source of energy. Without doubt, biofuel-based energy is a promising long-term energy source that can reduce the over dependence on fossil fuels as a result of feedstocks availability and renewability. However, biodiesel production from vegetable oil using the traditional homogeneous catalytic system is no longer defensible by industries in the near future, particularly due to food-fuel rivalry and ecological problems related to the conventional homogeneous catalytic system. This review presents a comprehensive step by step process of converting waste cooking oil (WCO) to biodiesel, using modified waste egg shell catalyst. The modified waste egg shell derived bi-functional catalyst could easily be removed from the fatty acid methyl esters (FAME) with limited environmental effects. The new modified catalytic system is able to convert the high free fatty acid (FFA) content waste cooking oil to FAME efficiently under moderate reaction conditions. Utilization of waste cooking oil as a feedstock for biodiesel production will reduce the food security issues that stem the biodiesel production from food-grade oil. Moreover, it will reduce the total production cost of the FAME due to its low cost. The major objective of this article is to demonstrate the current state of the use of heterogeneous bifunctional acid/base catalyst to produce biodiesel from green and non-edible waste cooking oil. At the end of the article, perspectives and future developments are also presented.

### 1. Introduction

The global energy crises are as a result of possible future depletion of conventional fossil fuels and current energy demand are the major drivers prompted the search for alternative renewable energy sources. Besides, fossil fuels are not eco-friendly as they are related to poisonous gases exhausts from automobile and industrial internal combustion engines, which eventually lead to global warming, acid rain and depletion of ozone layer [1–3]. Transportation of goods and services is an integral part of global economy, which depends solely on petroleum based sources of energy. Apart from coal, nuclear power, natural gas and hydroelectricity that serve at different capacity in the provision of energy, transport sector alone is more than 90% dependent on fossil fuels (petroleum), consuming more than 60% of total annual global fuel consumption [4–6]. Renewable sources of energy such as bio-fuels are

generally considered as replaceable alternative to traditional fossil fuels due to their feedstock availability and environmental friendly [7,8]. Biodiesel is one of the most promising alternative sources of energy considering its biodegradability and low emission of carbon dioxide, free sulphur and non-toxic nature [9–11]. Another interesting thing about biodiesel is that it possesses all the physico-chemical properties of traditional fossil fuel such as improved cetane number and high flash point [12,13].

As a result of rapid growth in human population, scientific and technological advancements in developing countries, the biodiesel demand is estimated to either doubled or tripled by the year 2020 and beyond. However, relevant studies have fully verified the number of issues regarding biodiesel that are not convincingly addressed yet. Conversion of triglycerides into FAME requires a reaction of the former with monohydric alcohol (methanol). Most of the researchers

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recommended the short chain monohydric alcohol, typically methanol, ethanol and propanol with no distinct justification of which provides the best viscosity requirements in line with specifications by American Society of Testing and Materials (ASTM) and European Standard (EN) or other related international agencies [13].

Technically, biodiesel is not yet considered as popular alternative source of energy to conventional fossil fuel worldwide due to its high cost of production, which is attributed to the cost of raw materials and labour, hence the fundamental policy of biodiesel is not yet achieved. Non availability of raw materials and effective catalytic system, are the major problems facing commercialization of biodiesel to meet the global demand and the united nation millennium environmental policy.

Edible vegetable oils i.e. palm oil, soybean oil, sunflower oil, etc. are the traditional feedstocks for the production of biodiesel. However, the high cost of feedstock which account for more than 80% of total production cost of biodiesel and possible hike in the prices of edible vegetable oils coupled with hunger threats as well as soil degradation associated with large scale farming for biodiesel feedstocks have on the other hand forced many agencies, particularly food and agricultural organizations to consider the option as non-reliable [14–17]. Non edible vegetable oil such as *Jatropha curcas* oil, castor oil, algae oil etc. could be considered as reliable feedstocks for the production of biodiesel in commercial scale [18–20]. Nevertheless, most of these crops are perennial in nature and their plantation could cause unnecessary deforestation in the near future which may affect the climatic condition of a particular region, hence un-economical and time consuming process [21]. Algae oil, even though considered as the most promising feedstock for biodiesel due to its high oil content and easy cultivation, but is also far from biodiesel production in commercial quantity due to the inadequate technical knowledge of cultivation and extraction of oil to commercial scale [13,22]. Waste cooking/ frying oil is one of the feedstock having dual advantage. A part from being low cost feedstock for biodiesel production, utilizing WCO as a feedstock, will further reduce water pollution for not been discharged into the water bodies [23].

## 2. Biodiesel as a future and promising alternative renewable energy source

Biodiesel or FAME is synthesized from renewable vegetable based oil or animal fat [23,24]. It is generally produced by the process of esterification or transesterification reaction of fatty acid or vegetable oil in the presence of monohydric alcohol, catalyst and temperature over the period of time [17,25]. The renewability, biodegradability and less toxicity are the most important features that made FAME globally acceptable as viable and sustainable fuel for the universe [12,26]. Biodiesel has the ability to work efficiently in similar way the traditional fossil fuels works in internal combustion engines [27–29]. Although FAME has some properties like pour point, flash point and cloud point a bit higher than the conventional fossil fuel, but still has similar cetane number and kinetic viscosity to that of normal diesel [30]. Consequently, protecting and prolonging the engine life due to its high lubricating property. The biodiesel properties (Table 1) are in agreement with the ASTM and EN specifications, hence, allow the commercialization of biodiesel worldwide.

## 3. Viability and socioeconomic impacts of biodiesel production from waste cooking oil

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 i.e. global warming and green house gas effects. Biodiesel is currently one of the most widely accepted alternative renewable sources of energy option to conventional fossil fuel. Nonetheless, biodiesel production cost remains the major issue today. Current commercial production of biodiesel

**Table 1**

Comparison of standards between biodiesel and fossil diesel, according to American Standard for Testing and Materials (ASTM) [29].

Fuel Property	Diesel	Biodiesel
Standard Method	ASTM D975	ASTM D6751
Fuel composition	Hydrocarbon(C10-C21)	FAME(C12-C22)
Cetane number	40–55	48–60
Density (g/cm <sup>3</sup> )	0.85	0.88
Cloud point (°C)	–15 to 5	–3 to 12
Flash point (°C)	60–80	100–170
Pour point (°C)	–30 to –15	–15 to 5
Carbon content (wt%)	87	77
Hydrogen content (wt%)	13	12
Oxygen content (wt%)	0	11
Sulphur content (wt%)	0.05	0.05
Water content (vol%)	0.05	0.05

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 [23,31]. The use of conventional feedstocks (edible oils) for biodiesel accounts for more than 80% of total biodiesel production cost. Hence, making biodiesel more expensive and therefore, not sustainable. Moreover, continual usage of traditional edible oils as feedstock for biodiesel may result to future food versus fuel competition thus, violating one of the cardinal objective of FAME production [32]. *Jatropha curcas* oil is particularly remarkable feedstock for FAME production, as it possess about 40% oil content and can grow on un-fertile soil thereby, avoiding competition with arable land for food crops, however *Jatropha curcas* seeds are toxic in nature, hence the harvest requires severe labour [33]. Recent studies suggested that the production cost of FAME could be reduced to halve through the utilization of WCO in comparison to the high grade vegetable oils [33]. About 15 million tons of waste cooking oil is annually been disposed in water or land across the globe. Such amount of low cost feedstock noteworthy special consideration, as it could bridge significant gap in current biodiesel demands [23]. Waste cooking oil, when properly utilized will produce biodiesel with less CO<sub>2</sub> emission at relatively low cost and thereby making it economically and socially viable as a renewable fuel. Besides that, converting WCO into FAME could help significantly in reducing the environmental pollution caused by its disposal into water bodies and land [34]. Nevertheless, some chemical changes occur to chemical properties of WCO as a result of heating at high temperature during cooking/ frying process which results to increase in the level of FFA and some impurities like water content. Basically fresh vegetable oil contained triglyceride, diglyceride, monoglyceride and free fatty acid (FFA) usually (< 1%). High FFA and water contents in the feedstock hampers FAME production due to subsequent soap formation when basic catalyst is used [30,35,36]. These challenges must be taken into consideration before using it as a feedstock for biodiesel production using base catalysts [37]. Different feedstocks for FAME production have different fatty acid composition and in turn can influence the biodiesel yield. Other fuel properties such as acid value, cetane number, cloud point, flash point, oxidation stability, cold filter and plugging point, kinematic viscosity could also be influence by FFA composition of the feedstock [38,39]. Basically, the vegetable based oils comprised of five major fatty acids components as presented in Table 2, namely, palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2) and linolenic (18:3).

WCO has so far been considered as one of the cheapest feedstock for biodiesel production, with dual advantage [35]. Utilizing it as feedstock for biodiesel is at the same time making the environment safe and cleaner for not being dispose into the water bodies that could pollute the water. Hence WCO is considered as economically and socially viable feedstock for low cost biodiesel production on a commercial scale.

**Table 2**  
Common fatty acid composition of plant based oil [36].

No.	Fatty acid	Formula	Structure	wt%
1.	Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	16:0	7.3
2.	Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	18:0	4.0
3.	Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	18:1	26.9
4.	Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	18:2	60.0
5.	Linolenic acid	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	18:3	0.5

#### 4. Preliminary investigations and pre-treatment of waste cooking oil

Low grade biodiesel feedstock, like WCO will undergo some preliminary investigations and preparations before subjecting it to FAME production [11]. Prior to subsequent biodiesel reactions, the collected WCO must be free from debris or other impurities through simple filtration technique [41]. The water content will subsequently be removed from WCO through drying with the aid of hot plate and stirrer at 120 °C. The FFA value greater than 1% is considered as higher FFA content and therefore not suitable for transesterification using basic catalysts [42]. Further pre-treatment stages are needed to employ for high FFA content of WCO (> 1%) in order to reduce the FFA value to < 1% before being transesterified to FAME, otherwise a saponification will occur which will greatly affect the biodiesel yield [43]. However, the pre-treatment stage previously employed to reduce the high FFA value of the feedstock before being subjected to transesterification reaction process is now considered as time and material consuming, which will make biodiesel production difficult and expensive, and therefore, new catalytic route of using modified heterogeneous solid bifunctional catalysts is now adopted in order to avoid the pre-treatment stage [44].

Basically, prior to embark on FAME production reaction, the number of investigative analysis of WCO needs to be carried out in order to know certain physico-chemical parameters of the feedstock (WCO). Acid value, saponification value and molecular weight of the feedstock are crucial points before either transesterification or esterification reaction. A simple titration method, usually in agreement with ASTM, EN and other scientifically accepted procedures are used to determine the aforementioned physico-chemical parameters of the said feedstock.

Acid value is the acid number contained in the oil sample. It is used to determine the FFA level in the oil sample. According to ASTM-D974 acid value is calculated using the formula below;

$$A.V = \frac{A \times M \times 56.1}{W} \quad (1)$$

where *A.V* is the acid value in (mg KOH/g), *A* is the amount of potassium hydroxide (KOH) consumed by the sample, *M* is the molar concentration of KOH and *W* is the weight of the oil in grams. Hence the FFA value is calculated using Eq. (2).

$$FFA = \frac{A.V}{2} \quad (2)$$

Saponification value indicates the amount of KOH needed to saponify 1 g of oil. It can be calculated using the formula in Eq. (3) according to ASTM D5558-95.

$$S.V = \frac{MM_{KOH}(B-S) \times M_{HCl}}{W} \quad (3)$$

where *S.V* is the saponification value, *B* is the volume of hydrochloric acid (HCl) in (ml) required by the blank, *S* is the volume of HCl in (ml) required by the sample, *MM* is the molar concentration of KOH, *M* is the molar concentration of HCl and *W* is the weight of the oil in (g). Saponification value plays an important role in determining the sample's molecular weight according to the formula in Eq. (4).

**Table 3**  
Some globally accepted vegetable oil analysis and their standard methods [42].

No.	Analysis	Method
1	Acid Value	AOAC (2000) 940.28
2	Carbon Residue	ASTM D4530-00
3	Density	ASTM D4052-96
4	Fatty acid composition	AOAC (2000) 963.33, 969.33
5	Iodine Value	EN 14111
6	Kinematic Viscosity	ASTM D 445-06
7	Oxidation Stability	EN 14112
8	Saponification Value	AOAS (1997)
9	Water Content	AOAC (1990)
10	Total Acid number	ASTM D 664-01

$$MW_{oil} = \frac{(56.1 \times 1000 \times 3)}{S.V} \quad (4)$$

where *MW<sub>oil</sub>* is the molar weight of the oil sample and *S.V* is the saponification value. The detailed procedures of these analyses were described in the Association of Official Agricultural Chemists (AOAC) method (2000). Zhang and Jiang [45] reported other globally accepted methods for vegetable oil analysis in Table 3.

Different studies have been conducted on WCO to produce biodiesel. Meng et al. [46] produced FAME from waste cooking oil using sodium hydroxide (NaOH) as a catalyst and methanol as reaction medium. The effects of different reaction parameters on conversion and quality of FAME were investigated. At the end of the study, 86% conversion under the optimum reaction conditions of 6:1 methanol to oil ratio, 0.7 wt% catalyst loading, 90 min reaction time and 50 °C reaction temperature were recorded. Similarly, Arquiza et al. [47] investigated the effect of operating parameters in the production of biodiesel from waste coconut oil using NaOH catalyst and methanol. Under the optimal reaction conditions of 60–65% reaction temperature, 0.5 wt% catalyst loading and 6:1 methanol to oil ratio, FAME yield of 94% was achieved. There are various reports of biodiesel production from waste cooking oil using conventional homogeneous catalyst, typically NaOH [48–50]. Hence, waste cooking oil is now considered as a reliable feedstock that could help in replacing the expensive edible oil for biodiesel production in commercial quantity.

#### 5. Catalysis of transesterification/esterification

Generally a catalyst is defined as any material or substance that speeds up the rate of chemical reaction by lowering its activation energy [51]. It is usually added in a minute amount in comparison to the quantity of the reactants, which is not consumed during the chemical reaction; it is also known as an initiator. 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 [52]. Catalysis generally represents the vital technology for accelerating essential chemical conversion, which is a key to recognize environmentally friendly and commercially feasible reactions for transforming energy carriers to directly usable energy. However, the use of heterogeneous catalysts for chemical conversions not only decreases the total energy input needed for production processes, but also improves two considerable catalyst aspects, i.e. selectivity and thermal stability, thus leading to ecologically benign green technology.

##### 5.1. Homogeneous catalysts for biodiesel production

Commercial production of biodiesel from vegetable oil relies solely on homogeneous catalysts considering their major advantage of reduced mass transfer resistance effect, hence faster reaction efficiency when compared to the heterogeneous catalysts. The homogeneous catalysts used in methanolysis could either be acidic or basic in nature.

Basic homogeneous catalysts are the most frequently used catalysts to assist 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 [53]. 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 most commonly used homogeneous catalysts for biodiesel production are hydroxides and alkoxides of alkali metals such as KOH, NaOH, sodium methoxide ( $\text{CH}_3\text{ONa}$ ) and potassium methoxide ( $\text{CH}_3\text{OK}$ ) [54,55]. In all of the listed homogeneous catalysts, KOH and NaOH are the most used catalysts for biodiesel production at commercial scale as a result of their ability to catalyze transesterification reaction at relatively low reaction temperature and high reaction rate which is about 4000 times faster than acid catalyst reaction rate [56]. High biodiesel yield could also be achieved at short reaction time, and most importantly, these catalysts are cheap and easy to get [53]. Several studies have been conducted on different feedstocks to produce biodiesel using homogeneous catalysts. Uzun et al. [55] 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 [57], 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. However, formation of soap and other unwanted emulsions as a result of presence of FFA content (> 1%) and other impurities from low grade feedstock is another problem that may hinder biodiesel yield [58]. The prominent homogeneous acid catalysts for methanolysis are mineral acids such as HCl and sulphuric acid ( $\text{H}_2\text{SO}_4$ ) [59]. Others are nitric acid ( $\text{HNO}_3$ ), aluminium chloride ( $\text{AlCl}_3$ ), organic sulfonic acid and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) [53]. Homogeneous acid catalysts generally have a slow reaction rate, and therefore, take long reaction time to esterify feedstock to biodiesel. Marchetti and Errazu [60] reported the biodiesel yield of 96% from model oil prepared using oleic acid and sunflower oil when  $\text{H}_2\text{SO}_4$  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. [61] reported that 98% yield of biodiesel was achieved when canola oil was subjected to methanolysis using  $\text{AlCl}_3$  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 can only use in food grades oils (palm oil, soybean oil etc.) as feedstock and therefore, making biodiesel production expensive. Moreover, homogeneous catalysts are peculiar to separation problems after the reaction process, which involves regular water washing that require a substantial amount of water and consequently, pollute the environment due to generation of acid water. Hence, homogeneous catalysts are not environmentally and economically benign for the sustainable biodiesel production at industrial scale.

## 5.2. Heterogeneous catalysts for biodiesel production

Heterogeneous catalysts are catalysts that are in different phase with the reacting medium in a reaction process. In biodiesel production, the feedstock and reaction medium, usually short chain alcohol (methanol) are in liquid phases, and the heterogeneous catalyst for the reaction in solid phase. With the emergence of solid heterogeneous catalysts for biodiesel production, most of the technical problems related to conventional homogeneous catalysts would be reduced. In recent years, heterogeneous catalysts are immensely receiving scientific and industrial attention, perhaps owing to their economic and environmental friendly. If properly utilized, heterogeneous catalysts would solve the post-reaction washing problems associated with the

homogeneous catalysts and therefore increasing the biodiesel yield [53]. Biodiesel production is deemed to be promoted and sustained economically, through proper usage of heterogeneous catalysts. Solid catalysts are in different phase with the reaction medium and therefore, facilitate it is separation from post reaction mixture [62]. Heterogeneous catalysts could successfully be separated from the reaction mixture via physical process, using either filtration or centrifuging method. Consequently, this would enable the reutilization of these catalysts more than once, as in the case of homogeneous catalysts, hence reducing the biodiesel cost [63,64]. Additionally, the level of dissolved metals or other elements ascending from catalyst in the produced biodiesel or glycerol could remarkably reduced when heterogeneous catalysts are properly utilized [53].

However, heterogeneous solid catalysts are also far from perfection as their counterpart homogeneous catalysts. Their major downside is low or limited catalytic active centers in comparison to the conventional homogeneous catalysts; consequently, necessitate the usage of severe reaction conditions in order to match the oil conversion related to what is obtained by homogeneous-catalysed biodiesel production [65]. Similarly, mass transfer resistance concerns associated to heterogeneous catalyst owing to the presence of two or three different phases (methanol, oil and solid catalyst) in the reaction mixture could be linked to slower reaction rate in the conversion of vegetable oil/lipid to biodiesel [66]. Heterogeneous catalysts require some preparatory processes for their synthesis, which are generally time-consuming. The high price of the materials needed for the synthesis of these catalysts would also make the biodiesel more expensive. Furthermore, poisoning of the catalytic active sites of the catalysts when exposed to the surrounding atmospheric medium could affect the stability and activity of some catalysts. Hence detail information regarding the physical and chemical properties of solid material is necessary. Presently, enormous scientific efforts are on course to develop stable and sustainable heterogeneous catalytic system that would ensure biodiesel production from low grade feedstock [53]. Heterogeneous catalysts could be basic or acidic in nature [62]. Both classes of heterogeneous catalysts could be utilized in alcoholysis process depending on the FFA content of the feedstock. Basic heterogeneous catalysts when properly manage could transesterify feedstock containing up to 3% FFA at mild reaction conditions in a single run process [67]. Heterogeneous solid acid catalysts could best esterify low grade oil such as palm fatty acid distillate (PFAD), lipids containing more than 85% FFA at mild reaction conditions [68]. Heterogeneous acid catalysts could transesterify low grade oil such as waste cooking oil containing high FFA at long reaction time and very high reaction temperature in a single run reaction process [69–71]. In order to avoid severe reaction conditions on the transesterification of low grade feedstock like waste cooking oil and jatropa oil, modified bifunctional heterogeneous catalysts that could perform both transesterification and esterification reaction processes simultaneously at mild conditions are highly recommended.

## 5.3. Solid base catalysts

Heterogeneous solid base catalysts constitute of alkaline metals and alkaline earth metals which made the group one and two of the periodic table. These basic materials have been utilized as heterogeneous catalysts for biodiesel production process. Heterogeneous base catalysts could be single alkaline earth metal oxides, supported alkali metal and alkaline earth metal oxides, mixed metal oxides, hydrotalcites and anionic ion-exchange resins.

Alkaline earth metal oxides catalysts, if properly modified have the capacity to assist transesterification reaction to feedstock containing low FFA (at least 3%) for a single run process, owing to their high basic strength. The basic strength of group II oxides and hydroxides is promoted with the increase in atomic number ranging from magnesium (Mg) to Barium (Ba), which significantly affects their catalytic capability to transesterify lipid feedstock [72].

The source of basic centers in alkaline earth metal oxides could be linked to the presence of  $M^{2+}$  and  $O^{2-}$  ion pair and surface hydroxyl group in a different coordination environment. The surface oxygen of these oxides could be affected by the surface composition of the solid catalysts and calcination temperature. Moreover, the specific surface area, degree of leaching in the reaction medium, basicity and selectivity during the transesterification reaction process must be considered as important factors in choosing the appropriate catalyst for biodiesel production [53]. The most commonly used basic heterogeneous catalyst for transesterification process is calcium oxide (CaO) [5]. 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 [73,74], crab shells [73], capiz shells [75], snail shells [76], mussel shells [77] and oyster shells [78] among others. Proper utilization of waste egg 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 formation of CaO catalyst [53]. Besides the economic advantages, the performance of CaO as a catalyst for biodiesel production could match the conventional homogeneous catalysts having achieved outstanding conversion yield over some selected feedstocks. Kawashima et al. [79] 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., [80] reported biodiesel yield of 86.75% from palm oil using obtuse horn derived CaO as a catalyst under the optimum reaction conditions of 5 wt% catalyst loading, 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 water ( $H_2O$ ) which would result in the formation of  $CaCO_3$  and  $Ca(OH)_2$  layers, respectively on the catalytic surface [81]. These effects distort and block the catalytic active sites hence lowering the activity of the catalysts and biodiesel yield [53].

Despite the encouraging results obtained using these catalysts, CaO catalyst alone could not transesterify low grade oil such as waste cooking oil and *Jatropha* oil. This is due to the presence of high FFA (> 3%) content 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 processes must be involved to reduce the FFA content to (< 3%). These processes are considered as time and resource consuming, making biodiesel production difficult and expensive. Hence, for the CaO catalyst to work successfully on low grade feedstock like waste cooking oil and *Jatropha* oil that have high FFA content (> 3%), there is need for further modification that will provide some acid centers 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 molybdenum trioxide ( $MoO_3$ ), tungsten trioxide ( $WO_3$ ), titanium dioxide ( $TiO_2$ ) and zirconate ( $ZrO_3$ ) possessed some acidic properties that would enhance the catalytic activity during transesterification of low grade feedstock like waste cooking oil.

#### 5.4. Solid acid catalysts

In recent years, 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 [82]. 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 [53,83,84]. It is generally assumed that biodiesel production reaction is similar for both homogeneous acid catalysts and heterogeneous acid catalysts, except that the heterogeneous acid catalysed reaction is influenced by the catalysts surface, which depends heavily on the interconnected system of large pores, surface acid sites and hydrophobicity [53]. 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 [30]

However, heterogeneous acid catalysts can only perform biodiesel production reactions under severe reaction conditions such as high reaction temperature, low reaction rate and long reaction period. 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 as presented in Table 4. Hence, the new route of catalytic system that can perform biodiesel production process on low grade feedstock under moderate reaction conditions is needed. Waste egg shell derived CaO supported by acidic transition metal oxides like  $WO_3$ ,  $MoO_3$ ,  $TiO_2$  when properly utilized could perform a transesterification reaction process on low grade feedstock like waste cooking oil at moderate reaction conditions. Most of the waste cooking oils are having between 2% and 15% FFA content [85,86] depending on how much the oil was used in frying purposes. About 85% of the waste cooking oil component are triglycerides, which undergo transesterification reaction during methanolysis, and the remaining component is FFA which undergoes esterification process during biodiesel production. The CaO catalyst would transesterify the triglycerides (TGs) and the acidic transition metal such as  $WO_3$ ,  $MoO_3$ ,  $ZrO_2$  or  $TiO_2$  will assist in esterifying the FFA content of the oil. Mixed oxide bifunctional catalysts could sustain biodiesel production from low grade feedstock at moderate reaction conditions (Table 5).

#### 5.5. Modified waste egg shell derived bifunctional catalyst

Generally, separation and waste water disposal problems, corrosion of biodiesel refining equipments increases concerned over the usage of heterogeneous catalysts [87,88]. Usage of solid heterogeneous catalysts for biodiesel production can overcome the separation problems. Heterogeneous basic 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 researches were conducted for transesterification reactions over these catalysts [80,89–92]. 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 [30].

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 bifunctional (having both acidic and basic properties). Bi-functional heterogeneous catalyst if utilized properly could perform both transesterification and esterification of TGs and FFA simultaneously under moderate reaction conditions, respectively. This is due to the fact that, bi-functional catalysts are having both basic and acidic sites and therefore can act as acid and base at the same time. Additionally, bi-

**Table 4**

A literature report on biodiesel production from different feedstocks using solid acid catalysts at severe reaction condition.

Catalyst	Preparation Method	Reaction conditions				Feedstocks	Yield (%)	Ref
		Temperature (°C)	Reaction Time (h)	Catalyst loading (wt%)	Methanol to oil molar ratio			
Al <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub> /WO <sub>3</sub>	Co-precipitation	175	1	4 g	40:1	Soybean	100	[77]
Zirconia supported HPA	Hydrolysis	200	5	3	20:1	Sunflower mustard	97	[78]
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	Precipitation	260	1	3	40:1	Sesame oil	92	[22]
CsHPW	Precipitation	200	10	3	20:1	Oleic acid-Soybean mixture	90.4	[79]
WO <sub>3</sub> /ZrO <sub>2</sub>	Impregnation	75	20	Not specified	19.4:1	Not specified	85	[80]
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /ZnO	Sol-gel	200	8	5	Not specified	Colza oil	93.7	[61]
Mn <sub>3.5</sub> Zr <sub>0.5</sub> Al <sub>x</sub> O <sub>3</sub>	Co-precipitation	150	5	2.5	14:1	WCO	> 93	[62]
Ar-SBA-15	Direct mixing	140	2	6	20:1	Crude palm oil	90	[81]
Sulfated ZrO <sub>2</sub>	Impregnation	180	1	3	3:1	Dodecanoic acid	96	[60]
Ar-SBA-15	Not reported	260	2.5	1	20:1	Crude palm oil	90	[81]
VOPO4.2H2O	Not reported	150	1	2	1:1	Used cooking oil	80%	[60]
Carbonized and Sulfated asphalt	Carbonization	260	1	2.5	18.2:1	Waste cooking oil	89.9	[82]
SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -SiO <sub>2</sub>	Impregnation	200	3	4	9:1	Used cooking oil	90	[83]
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -SiO <sub>2</sub>	Impregnation	150	3	4	15:1	Waste cooking oil	> 92.3	[84]
ZrO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup>	Sulfonation	200	1	1	6:1	Palm kernel	90.3	[85]
Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> /ZnO	Co-mixing	200	6	8	1:1	Colza oil	93.7	[86]
TiO <sub>2</sub> /SO <sub>4</sub> <sup>2-</sup>	Precipitation	230	2	8	12:1	Coconut oil Cotton oil	86.3 90	[81]
ZnO	Not reported	300	3	1	6:1	Soybean	80	[85]
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /TiO <sub>2</sub> /La <sup>3+</sup>	Precipitation	200	5	2	15:1	Not reported	90	[61]
Al <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub> /WO <sub>3</sub>	Wet impregnation	200	20	4 g	4.5:1	Soybean oil	> 90	[21]

functional catalysts can easily be modified to introduce the needed physicochemical properties that could easily overcome the problem of high FFA and water content present in the low grade feedstock like waste cooking oil during the transesterification reaction [44]. Hence, modified waste egg shell derived bifunctional heterogeneous catalysts could be promising alternative catalysts to overcome the problems associated 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 5. In this study, similar catalyst with bifunctional capability would be synthesized using transition metal oxides (WO<sub>3</sub>, ZrO<sub>2</sub>, MoO<sub>3</sub> etc.) supported on CaO from the waste egg shell and employ for biodiesel synthesis from WCO.

## 6. Preparation methods of bifunctional solid catalysts

Mixed oxides bifunctional heterogeneous catalysts can be synthesized through different catalyst preparatory methods such as; wet impregnation method [90], co-precipitation method [29], sol gel method

**Table 5**

A literature report on biodiesel production from high FFA feedstocks using bifunctional catalysts under mild conditions.

Catalyst	Preparation Method	Reaction conditions				Feedstocks	Yield (%)	Ref
		Temperature (°C)	Reaction Time (h)	Catalyst loading (wt%)	Methanol to oil molar ratio			
CaO/La <sub>2</sub> O <sub>3</sub>	Co-precipitation	65	6	4	24:1	Jatropha curcas oil	86.51	[27]
Bi <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub>	Impregnation	150	4	2	15:1	Jatropha curcas oil	93	[6]
Mo-Mn <sup>IV</sup> -Al <sub>2</sub> O <sub>3</sub> -15 wt% MgO	Wet Impregnation method	100	4	4 g	27:1	Waste cooking oil	91.4	[40]
Mn <sub>3.5</sub> Zr <sub>0.5</sub> Al <sub>x</sub> O <sub>3</sub>	Co-precipitation	150	5	2.5	14:1	Waste cooking oil	> 93	[66]
Cs-Zr/Al <sub>2</sub> O <sub>3</sub>	Impregnation	65	3	3	20:1	Waste cooking oil	90	[15]
CaO-ZrO <sub>2</sub>	Impregnation	65	2	10	30:1	Waste cooking oil	92.1	[64]
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -SiO <sub>2</sub>	Impregnation	150	3	4	15:1	Waste cooking oil	> 92.3	[87]

[69] and physical mixing/co-mixing [93] depending on the precursor of the metal oxides. These preparatory methods are not only simple and easy, but economically feasible as does not involve high technical complex procedures that would make the synthesis difficult and expensive. Biomass based bifunctional catalyst involves the use of simple waste material (waste egg shell, palm kernel shell etc.) and few chemicals. These catalysts are ecofriendly and therefore, reduced environmental hazards greatly through biodegradation process. The feasible techniques for the synthesis of these catalysts are fully discussed below.

### 6.1. Wet impregnation method

The wet impregnation method is one of the easiest methods of catalyst preparation. During wet impregnation catalyst synthesis, the precursors usually in salt form or salt and oxide forms are mixed together in a beaker with distilled water and stirred for at least five to six hours. After while the resultant slurry would be dried at 110 °C for 24 h in an oven. The dried sample would be calcine in a furnace at

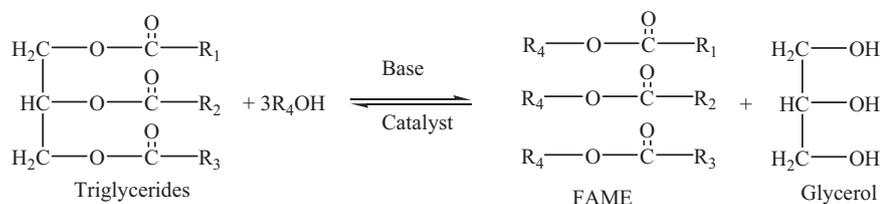


Fig. 1. General equation for transesterification reaction of biodiesel synthesis from triglycerides [49].

appropriate temperature [90,93]. The wet impregnation method is very simple and effective in synthesizing supported catalyst as it could be able to fabricate several active sites on the surface of catalyst which are favourable in transesterification/esterification reaction processes.

### 6.2. Co-precipitation method

Co-precipitation/precipitation method of catalyst synthesis involves dissolution of catalyst precursors usually salt precursors into distilled water and then stirred vigorously. To this mixture, precipitating agents usually alkaline, such as ammonium hydroxide (NH<sub>4</sub>OH), KOH, NaOH, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) is added to precipitate the solution at constant stirring for 3 h and the pH of the solution is maintained at 10. The resultant precipitate would be dried in oven at 110 °C over night, after which the dried sample would be calcine in the furnace at appropriate temperature [29,93]. This method could be able to facilitate the development of bimetallic oxide supported CaO catalyst exhibiting highly acidic or basic property due to synergetic effect from the two or three metal oxides involved.

### 6.3. Sol gel method

Sol gel method is another technique used for catalyst synthesis, which involves the mixing of butyl titanate and anhydrous ethanol in drop wise to another solution of deionized water, anhydrous ethanol, nitric acid and appropriate amount of nitrate precursor at room temperature under vigorous stirring to carry out hydrolysis. A yellowish transparent sol would form after constant stirring for 3 h. The sol would be dried at 80 °C for 24 h to form xero-gel which would subsequently crush and sieve to 60–100 mesh and then calcine at appropriate temperature in the furnace [69].

### 6.4. Physical mixing method

The physical mixing method involves mixing and grinding of pure metal oxides together using agate mortar. The oxides are usually mixed with distilled water in a beaker and stirred constantly for five hours. The resulting slurry would be calcine at an appropriate temperature in a

furnace [93].

## 7. Physical and chemical characterization of modified waste egg shell derived CaO catalysts for biodiesel production from waste cooking oil

In order to ascertain the catalytic activity of the heterogeneous mixed oxide catalysts, quite number of laboratory characterizations and other relevant analysis must be carried out. The acidic and basic properties of the catalyst could be determined using ammonia temperature program desorption (TPD-NH<sub>3</sub>) and carbon dioxide temperature program desorption (TPD-CO<sub>2</sub>), respectively [7]. The surface area and pore size of the catalyst is measured by Brunauer-Emmett-Teller (BET) specific surface analysis [39,94]. Crystallography, elemental composition and functional group analysis determinations are carried out by X-ray diffraction (XRD), X-ray fluorescent (XRF), energy dispersive X-ray spectrometry and Fourier transform infrared (FTIR), respectively [8,90]. It is generally known that, the calcination process of the solid heterogeneous catalysts in the form of carbonate or hydroxide will maximize the active sites responsible for the catalyzation of transesterification reaction. The appropriate calcination temperature of mixed oxide catalysts is determined by thermal gravimetric analysis (TGA) which measures the thermal stability of the sample [58]. The morphology of the catalyst is obtained by scanning electron microscope (SEM) [8,58]. With regard to catalyst leaching, which is peculiar to most of the metal oxides particularly alkali earth metal oxides, atomic absorption spectroscopy (AAS) is used to measure the level of leached elements into biodiesel product [95].

## 8. Biodiesel synthesis processes

Biodiesel or FAME is generally produced by the transesterification reaction of TGs or esterification reaction of FFA. During transesterification reaction process, 1 mol of triglycerides react with 3 mol of methanol in the presence of catalyst and temperature to produce 3 mol of methyl ester (biodiesel) and glycerol as presented in Fig. 1. Chan and Fang [96,97] reported that the transesterification reaction can be formulated in three step reaction processes as depicted in Fig. 2.

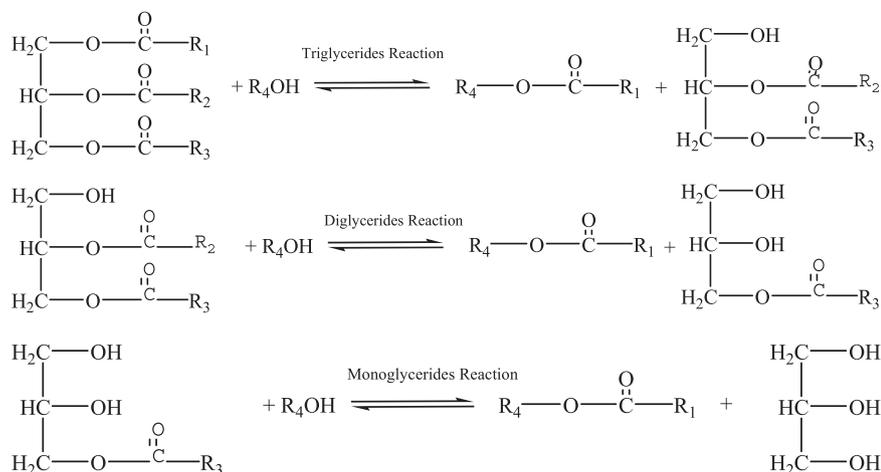


Fig. 2. Three step equations for transesterification reaction process of biodiesel production from triglycerides [49].

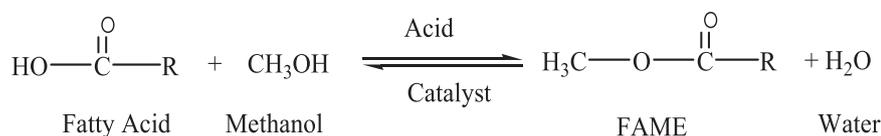


Fig. 3. General equation for the esterification reaction of biodiesel production from a fatty acid.

Transesterification reaction is reversible reaction process and therefore requires high amount of methanol in order to move the reaction forward [53]. The excess methanol and glycerol produced together with FAME at the end of the reaction could be separated using centrifuge [98]. Transesterification reaction rate using solid base catalyst is faster than esterification reaction using solid acid catalyst. This is due to the slower reaction rate of solid acid catalyst resulting from lower degree of catalyst contact with oil and methanol [96].

In esterification reaction 1 mol of free fatty acid reacts with 1 mol of methanol in the presence of an acid catalyst to produce 1 mol of FAME and water as shown in Fig. 3. Chen and Fang [96].

## 9. Reaction conditions and their effect on biodiesel yield

Biodiesel production reaction occurs under different reaction conditions like temperature, which has effects on calcination of the catalyst and biodiesel reaction, methanol to oil molar ratio, reaction time and catalyst loading, all of which have different effects on biodiesel production process. In order to obtain a higher biodiesel yield with fulfilled standard specification, these conditions must be optimized during the reaction process.

### 9.1. Effect of calcination temperature

Calcination temperature plays enormous role in catalyst synthesis, through the development of the major catalytic properties such as basic and acidic site densities, surface area, pore volume as well as molecular and crystalline structure. During calcination process, catalysts are subjected to high temperature which exposes the catalytic sites by eliminating the loosely bound carbon dioxide and water molecules and also rearranges the bulk atoms on surface of the catalyst [70]. Park Y-M, et al., [99] reported the increase in FAME yield from 62% to 90% when the calcination temperature was varied from 250 °C to 350 °C for 4 h. This is due to the increase in calcination temperature to 350 °C which enhance the catalyst performance for transesterification process. However, excessive increase in calcination temperature during the catalyst synthesis may results to decrease in FAME yield, signifying low catalytic performance. This might be due to the gaseous diffusion out of the pores during the thermal treatment resulting to surface pores limitation or partial removal of the binding water molecules from catalyst structure which may lead to damage of the catalyst and subsequently form unknown species [71,100].

### 9.2. Effect of catalyst loading

Catalyst is generally believed to speed up the reaction process by lowering the activation energy. Conversion of triglycerides or lipids to biodiesel involves the use of catalysts which speeds up the reaction process by lowering the needed activation energy. Lower catalyst loading is usually applied in the initial stage of the reaction and the conversion yield is measured. The subsequent catalyst loading will be increased periodically at constant reaction conditions until the best biodiesel yield is achieved. Amani et al. [71] reported the high FAME yield of 90% with increase in catalyst loading to 3 wt% after 3 h reaction time which was considered as optimum catalyst loading for the reaction. Biodiesel yield was decreased to 83% when the catalyst loading was increased to 4 wt%. Low catalyst loading could result to methanol solubility in low grade feedstock like waste cooking oil [99].

### 9.3. Effect of methanol to oil molar ratio

Methanol to oil molar ratio is one of the four reaction parameters for the biodiesel production reaction. This parameter plays an important role both in transesterification and esterification reaction process. During esterification of high FFA oil to biodiesel, which is reversible reaction process, excess methanol is necessary in order to increase the reaction rate and biodiesel yield [101]. Conversions of TGs to FAME occur when it reacts with the active site of the catalyst. At a molecular stage, TGs are protonated at the carbonyl group to form the carbonation ion, which can undergo a reaction to form esters [30]. Nevertheless, active sites are flooded with excess methanol which hinders the protonated TGs. Yan Li et al. (2010) reported that 90% of biodiesel yield was achieved at the maximum of 15:1 methanol to oil molar ratio. No significant increase in biodiesel yield was observed from 15:1 to 18:1 methanol to oil molar ratio hence 15:1 was adopted in view of economics and methanol recovery after the reaction [70]. The high amount of methanol during methanolysis was reported to be problematic during separation process. This is due to the formation of emulsion from ester layer and glycerol layer formed. The polar nature of the methanol made it to act as emulsifier which enhances the formation of emulsion [101]. However, it is generally concluded that excess methanol increases the production yield and also enhances the interaction between TGs molecules and catalyst [102,103].

## 10. Alternative techniques for biodiesel production

Biodiesel can be produce popularly by esterification process of FFA or transesterification process of TGs using different techniques. High renewable energy demand requires more advanced techniques such as microwave, autoclave and ultrasound reactors for the production of biodiesel in commercial scale.

### 10.1. Conventional reflux method

Conventional reflux method is one of the most commonly used technique for biodiesel production, which is equipped with two or three neck round bottom flask placed in an oil bath on stirring hot plate and a water cool condenser; the setup is placed in a fume-cupboard during the biodiesel production process. However, low or moderate reaction temperature and lower pressure are considered as the major setback to this technique. Hence, using reflux method for biodiesel reaction that occur at normal pressure and sufficiently high temperature could not be achieved [30]. Slow reaction rate was also observed in conventional reflux method which occurs as a result of energy transfer that depends on conventional current and thermal conductivity of the reaction mixture [104]. The conventional normal reflux set up is presented in Fig. 4.

### 10.2. Autoclave reactor

Autoclave reactor is the general reactor for biodiesel production reaction processes. It could be applicable to high temperature and pressure esterification reaction using acid catalysts. The pressure and reaction temperature could be greater than the boiling point of the methanol because it provides closed system reaction. More importantly, the reaction temperature, pressure, feedstock or alcohol flow and stirring speed could be monitored and controlled on the computer program [94,98], hence, low and moderate temperature transesterification

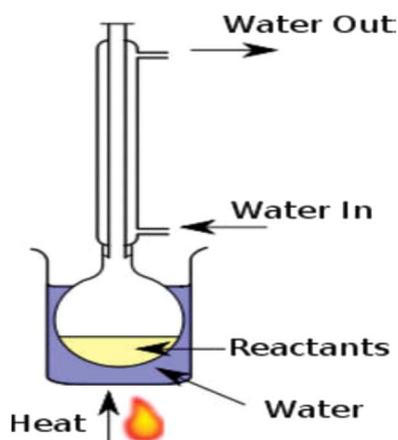


Fig. 4. Schematic diagram of conventional reflux setup for the biodiesel production [33].

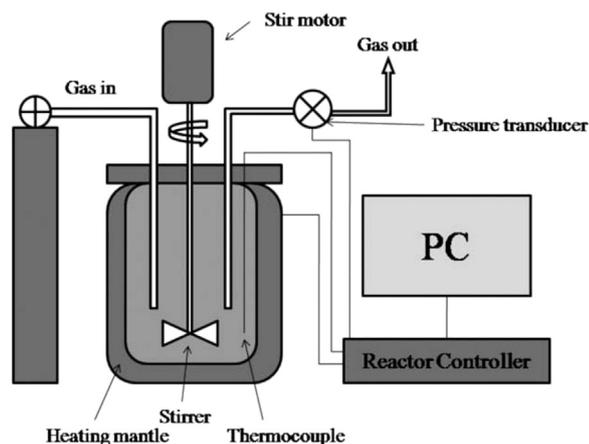


Fig. 5. Schematic diagram of autoclave reactor for biodiesel production [28].

reaction is also applicable to this reactor. However, the major setback of this reactor is that it requires regular maintenance and consume large amount of electricity which could possibly make biodiesel more expensive [30]. The schematic diagram of typical Autoclave reactor is displayed in Fig. 5.

## 11. Biodiesel quantitative analysis

Gas chromatography and flame ionization detector (GC-FID) is the combined equipment used for the determination of the composition of FAME from biodiesel, which is in accordance with the EN 14103 procedure. The GC setup is made up of HP-INNOWax polar capillary column with the length of 30 m and a thickness of 5  $\mu\text{m}$  with the internal diameter of 0.33 mm; the carrier gas and the internal standard of FID is Helium gas. During the GC-FID analysis 1  $\mu\text{L}$  of each sample is usually mixed with methyl heptadecanoate as internal standard and injected manually. The starting temperature is 50  $^{\circ}\text{C}$ , the initial rate is 15  $^{\circ}\text{C}/\text{min}$  up to 180  $^{\circ}\text{C}$  followed by second rate at 17  $^{\circ}\text{C}/\text{min}$  up to 230  $^{\circ}\text{C}$  and finally from the rate of 30  $^{\circ}\text{C}$  up to 380  $^{\circ}\text{C}$  with a holding time of 10 min [94,98,101].

Simple formulas were proposed by Wan Omar and Amin, Guo et al. [105,106] to calculate the percentage yield of methyl ester and Nascimento et al. [107] to calculate the percentage of FFA conversion when high FFA feedstock is used for biodiesel production. The two suggested formulas are displayed in Eqs. (5) and (6), respectively.

$$\text{Methylester (\%)} = \frac{\% \text{FAME Area from GC} \times \text{weight of product}}{\text{weight of feedstock used}} \times 100\% \quad (5)$$

$$\text{Conversion of FFA (\%)} = [1 - (\text{Final Acid value} / \text{Initial Acid value})] \times 100\%. \quad (6)$$

## 12. Conclusion

Conventional production of biodiesel from edible oil such as soybean oil, palm oil over traditional (homogeneous) catalytic system could no longer be sustained as an alternative source of energy, considering the future food versus fuel competition. Besides, food grade vegetable oils are very expensive, and more than 80% of total production cost of biodiesel is accounted for the feedstock used. Non edible oils such as waste cooking oil, *jatropha curcas* oil, animal fats and grease, are considered as sustainable feedstocks for biodiesel production considering their availability and low cost. Research shows that the production cost of FAME could be reduced to halve through the utilization of waste cooking oil as feedstock in comparison to the food grade vegetable oils. Hence waste cooking oil could be a viable and sustainable feedstock for FAME production due to its low cost. Nevertheless, the category of these feedstocks is considered as low grade oils due to the presence of impurities such as moisture and high FFA content ( $> 1\%$ ). Conventional catalytic system (homogeneous catalyst) is another problem facing the commercialization of biodiesel production due to its separation and other environmental related problems after the reaction. The homogeneous catalyst system forms soap on high FFA feedstock and therefore reduces the biodiesel yield at the end of the reaction. Heterogeneous solid base catalysts are only suitable for low grade feedstock containing  $< 3\%$  FFA, otherwise, multiple steps transesterification reaction process is necessary. Solid acid catalyst is also far from perfection as it can only convert triglycerides to biodiesel under severe reaction conditions (high temperature and long reaction time). This study discussed new catalytic system from bio source (waste egg shell) incorporated in transition metal oxides that could make an excellent bifunctional heterogeneous catalyst, that is renewable, biodegradable with least environmental effects, and could convert waste cooking oil to FAME under moderate reaction conditions. The step by step processes of FAME production from waste cooking oil were also discussed. FAME production from waste cooking oil over modified waste egg shell catalyst would make a sustainable and low cost alternative renewable source of energy with less environmental effect.

## 13. Future direction

Considering the current global energy demand, there is an urgent need to diversify into other alternative 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 now considered as the best option to conventional fossil fuels due to its biodegradability, less toxic and similar performance with 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 used as a feedstock and the conventional catalytic system which is associated with separation problems. These problems could only be solved through the reduction of cost of production and better catalytic systems.

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 a feedstock for FAME production will reduce the production cost to halve when compared to high grade vegetable oil.

The heterogeneous solid based catalyst could serve as the best option to a homogeneous catalyst for the commercial FAME production

considering the easy separation/removal of the catalyst after the reaction. Modified waste egg shell incorporated in transition metal oxides could serve as the best catalytic system for FAME production from waste cooking oil under moderate reaction conditions, regardless of the of high FFA and moisture content in waste cooking oil.

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## References

- [1] Muhammad Y, Adeniyi P, Raji-yahya AO, Aziz ARA, Mohd W, Wan A. Acidity and catalytic performance of Yb-doped SO<sub>2</sub> for biodiesel production. *J Taiwan Inst Chem Eng* 2015;000:1–10.
- [2] Maeda H, Hagiwara S, Nabetani H, Sagara Y, Soerawidjaya TH, Tambunan AH, et al. Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: a kinetic study. *Renew Energy* 2008;33:1629–36.
- [3] Chouhan APS, Sarma AK. Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renew Sustain Energy Rev* 2011;15:4378–99.
- [4] Piriou B, Vaitilingoma G, Veysiere B, Cuq B, Rouau X. Potential direct use of solid biomass in internal combustion engines. *Prog Energy Combust Sci* 2013;39:169–88.
- [5] Borges ME, Diaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review. *Renew Sustain Energy Rev* 2012;16:2839–49.
- [6] Avhad MR, Marchetti JM. A review on recent advancement in catalytic materials for biodiesel production. *Renew Sustain Energy Rev* 2015;50:696–718.
- [7] Rabiah Nizah MF, Taufiq-Yap YH, Rashid U, Teo SH, Shajaratun Nur ZA, Islam A. Production of biodiesel from non-edible *Jatropha curcas* oil via transesterification using Bi2O3-La2O3 catalyst. *Energy Convers Manag* 2014;88:1257–62.
- [8] Shajaratun Nur ZA, Taufiq-Yap YH, Rabiah Nizah MF, Teo SH, Syazwani ON, Islam A. Production of biodiesel from palm oil using modified Malaysian natural dolomites. *Energy Convers Manag* 2014;78:738–44.
- [9] Yaakob Z, Mohammad M, Alherbawi M, Alam Z, Sopian K. Overview of the production of biodiesel from waste cooking oil. *Renew Sustain Energy Rev* 2013;18:184–93.
- [10] Hafidz A, Fauzi M, Aishah N, Amin S. Optimization of oleic acid esterification catalyzed by ionic liquid for green biodiesel synthesis. *Energy Convers Manag* 2013;76:818–27.
- [11] Mardhiah HH, Chyuan H, Masjuki HH, Lim S, Lee HV. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renew Sustain Energy Rev* 2017;67:1225–36.
- [12] Nigam PS, Singh A. Production of liquid biofuels from renewable sources. *Prog Energy Combust Sci* 2011;37:52–68.
- [13] Galadima A, Muraza O. Biodiesel production from algae by using heterogeneous catalysts: a critical review. *Energy* 2014;78. (0–11).
- [14] Na H, Jeong D, Jang W, Shim J. The effect of preparation method on Fe / Al / Cu oxide-based catalyst performance for high temperature water gas shift reaction using simulated waste-derived synthesis gas. *Int J Hydrog Energy* 2015;40:12268–74.
- [15] Patle DS, Sharma S, Ahmad Z, Rangaiah GP. Multi-objective optimization of two alkali catalyzed processes for biodiesel from waste cooking oil. *Energy Convers Manag* 2014;85:361–72.
- [16] Amani H, Ahmad Z, Hameed BH. Highly active alumina-supported Cs – Zr mixed oxide catalysts for low-temperature transesterification of waste cooking oil. *Appl Catal A Gen* 2014;487:16–25.
- [17] Yan S, Salley SO, Ng KYS. Simultaneous transesterification and esterification of unrefined or waste oils over ZnO-La 2 O 3 catalysts. *Appl Catal A Gen* 2009;353:203–12.
- [18] Huerga IR, Zanuttini MS, Gross MS, Querini CA. Biodiesel production from *Jatropha curcas*: integrated process optimization. *Energy Convers Manag* 2014;80:1–9.
- [19] Pua F, Fang Z, Zakaria S, Guo F, Chia C. Direct production of biodiesel from high-acid value *Jatropha* oil with solid acid catalyst derived from lignin. *Biotechnol Biofuels* 2011;56:2–9.
- [20] Banković-Ilić IB, Stamenković OS, Veljković VB. Biodiesel production from non-edible plant oils. *Renew Sustain Energy Rev* 2012;16:3621–47.
- [21] Supamathanon N, Wittayakun J, Prayoonpokarach S. Properties of *Jatropha* seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. *J Ind Eng Chem* 2011;17:182–5.
- [22] Nautiyal P, Subramanian KA, Dastidar MG. Kinetic and thermodynamic studies on biodiesel production from *Spirulina platensis* algae biomass using single stage extraction – transesterification process. *Fuel* 2014;135:228–34.
- [23] Lee AF, Bennett JA, Manayil JC, Wilson K. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *Chem Soc Rev* 2014;43:7887–916.
- [24] Furuta Satoshi, Hiromi Matsushashi, Kazushi A. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catal Commun* 2004;5:721–3.
- [25] Shin H, An S, Sheikh R, Park YH, Bae S. Transesterification of used vegetable oils with a Cs-doped heteropolyacid catalyst in supercritical methanol. *Fuel* 2012;96:572–8.
- [26] Meher LC, Churamani CP, Ahmed Z, Naik SN. *Jatropha curcas* as a renewable source for bio-fuels — a review. *Renew Sustain Energy Rev* 2013;26:397–407.
- [27] Hwa S, Goto M, Taufiq-yap YH. Biodiesel production from *Jatropha curcas* L. oil with Ca and La mixed oxide catalyst in near supercritical methanol conditions. *J Supercrit Fluids* 2015;104:243–50.
- [28] Islam A, Taufiq-yap YH, Chan E, Moniruzzaman M, Islam S. Advances in solid-catalytic and non-catalytic technologies for biodiesel production. *Energy Convers Manag* 2014;88:1200–18.
- [29] Taufiq-yap YH, Hwa S, Rashid U, Islam A, Zobir M. Transesterification of *Jatropha curcas* crude oil to biodiesel on calcium lanthanum mixed oxide catalyst: effect of stoichiometric composition. *Energy Convers Manag* 2014;88:1290–6.
- [30] Lokman IM, Rashid U, Yunus R, Taufiq YH. Carbohydrate-derived solid acid catalysts for biodiesel production from low-cost feedstocks: a review. *Catal Rev Sci Eng* 2014;56:187–219.
- [31] Lee AF, Bennett JA, Manayil JC, Wilson K, Lee AF. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *R Soc Chem* 2014:1–30.
- [32] Sarin R, Sharma M, Sinharay S, Malhotra RK. *Jatropha – palm biodiesel blends: an optimum mix for Asia*. *Fuel* 2007;86:1365–71. <http://dx.doi.org/10.1016/j.fuel.2006.11.040>.
- [33] Escobar JC, Lora ES, Venturini OJ, Yáñez EE, Castillo EF, Almazan O. Biofuels: environment, technology and food security. *Renew Sustain Energy Rev* 2009;13:1275–87.
- [34] Daniel C, Araújo M De, Andrade CC De, Souza E De, Dupas FA. Biodiesel production from used cooking oil: a review. *Renew Sustain Energy Rev* 2013;27:445–52.
- [35] Tuong T, Tran V, Kaiprommarat S, Kongparaku S, Reubroycharoen P, Guan G, et al. Green biodiesel production from waste cooking oil using an environmentally benign acid catalyst. *Waste Manag* 2016;52:367–74.
- [36] Atadashi IM, Aroua MK, Aziz ARA, Sulaiman NMN. The effects of water on biodiesel production and refining technologies: a review. *Renew Sustain Energy Rev* 2012;16:3456–70.
- [37] Rashid U, Ibrahim M, Yasin S, Yunus R, Taufiq-Yap YH, Knothe G. Biodiesel from *Citrus reticulata* (Mandarin orange) seed oil, a potential non-food feedstock. *Ind Crop Prod* 2013;45:355–9.
- [38] Motasemi F, Ani FN. A review on microwave-assisted production of biodiesel. *Renew Sustain Energy Rev* 2012;16:4719–33.
- [39] Nakajima K, Hara M. Amorphous Carbon with SO 3H Groups as a Solid Brønsted Acid Catalyst. *Am Chem Soc Catal* 2012;2:1296–304.
- [40] Muppaneni T, Reddy HK, Ponnusamy S, Patil PD, Sun YQ, Dailey P. SGD. Optimization of biodiesel production from palm oil under supercritical ethanol conditions using hexane as co-solvent: a response surface methodology approach. *Fuel* 2013;107:633–40.
- [41] Agarwal D, Agarwal AK. Performance and emissions characteristics of *Jatropha* oil (preheated and blends) in a direct injection compression ignition engine. *Appl Therm Eng* 2007;27:2314–23.
- [42] Sherbiny SA El, Refaat AA, Elsheltawy ST. Production of biodiesel using the microwave technique. *J Adv Res* 2010;1:309–14.
- [43] Alves CT, Oliveira A, Carneiro SAV, Silva AG, Andrade HMC, Melo SABV De, et al. Transesterification of waste frying oil using a zinc aluminate catalyst. *Fuel Process Technol* 2013;106:102–7.
- [44] Farooq M, Ramli A, Subbarao D. Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *J Clean Prod* 2013;59:131–40.
- [45] Zhang J, Jiang L. Acid catalysed esterification of *Zanthoxylum bungeanum* oil with high free fatty acids for biodiesel production. *Bioresour Technol* 2008;99:8995–8.
- [46] Meng X, Chen G, Wang Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Process Technol* 2008;9:851–7.
- [47] AC A, MC B, R T. Production of biodiesel and oleochemicals from used frying oil. Los Banos: University of Philippines; 2000.
- [48] P F, MJN C, I R, JF M, R B, J B. Production of biodiesel from waste frying oil. *Waste Manag* 2006;26:487–94.
- [49] X Y, H M, Q Y, Z W, J C. Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflower oil. *Appl Energy* 2012;91:320–5.
- [50] Y G, YCL, CP K. A clean biodiesel fuel produced from recycled oils and grease trap oils. *Better air Qual. Asian Pacific rim cities*. 1–6. BAQ, Hong Kong: Polytechnic University; 2002. p. 55.
- [51] Peter Atkins Fellow of Lincoln College, University of Oxford, Oxford U, Julio De Paula Professor of Chemistry, Lewis and Clark College, Portland, Oregon U. *Physical Chemistry*. Ninth. New York: W,H Freeman and Company New York; 2010.
- [52] Ertl G, Knözinger H, Weitkamp J. Preparation of solid catalysts. John Wiley & Sons; 2008.
- [53] Avhad MR, Marchetti JM. Innovation in solid heterogeneous catalysis for the generation of economically viable and ecofriendly biodiesel: a review. *Catal Rev* 2016;4940:1–52.
- [54] Dias JM, M.C.M A-F, Almeida MF. Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality. *Fuel* 2008;87:3572–8.
- [55] Uzun BB, Kılıç M, Özbay N, Pütün AE, Pütün E. Biodiesel production from waste frying oils: optimization of reaction parameters and determination of fuel

- properties. *Energy* 2012;44:347–51.
- [56] Baskar G, Aiswarya R. Trends in catalytic production of biodiesel from various feedstocks. *Renew Sustain Energy Rev* 2016;57:496–504.
- [57] Fadhil AB, Ali LH. Alkaline-catalyzed transesterification of *Silurus triostegus* Heckel fish oil: optimization of transesterification parameters. *Renew Energy* 2013;60:481–8.
- [58] Nur Syazwani O, Rashid U, Taufiq Yap YH. Low-cost solid catalyst derived from waste *Cyrtopleura costata* (Angel Wing Shell) for biodiesel production using microalgae oil. *Energy Convers Manag* 2015;101:749–56.
- [59] Rashid U, Anwar F. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel* 2008;87:265–73.
- [60] Marchetti JM, Errazu AF. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. *Biomass Bioenergy* 2008;32:892–5.
- [61] Soriano NU, Venditti R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification. *Fuel* 2009;88:560–5.
- [62] Al-jammal N, Al-hamamre Z, Alnaief M. Manufacturing of zeolite based catalyst from zeolite tuff for biodiesel production from waste sun flower oil. *Renew Energy* 2016;93:449–59.
- [63] Tonetto GM, Marchetti JM. Transesterification of soybean oil over  $\text{Me}/\text{Al}_2\text{O}_3$  ( $\text{Me} = \text{Na}, \text{Ba}, \text{Ca}, \text{and K}$ ) catalysts and monolith  $\text{K}/\text{Al}_2\text{O}_3$ -cordierite. *Top Catal* 2010;53:755–62.
- [64] Sánchez-Cantú M, Pérez-Díaz LM, Pala-Rosas I, Cadena-Torres E, Juárez-Amador L, Rubio-Rosas E, Rodríguez-Acosta M, Valente JS. Hydrated lime as an effective heterogeneous catalyst for the transesterification of castor oil and methanol. *Fuel* 2013;110:54–62.
- [65] Kazemian H, Turowec B, Siddiquee MN, Rohani S. Biodiesel production using cesium modified mesoporous ordered silica as heterogeneous base catalyst. *Fuel* 2013; n.d. p. 719–24.
- [66] Thitsartarn W, Kawi S. Transesterification of oil by sulfated Zr-supported mesoporous silica. *Ind Eng Chem Res* 2011;50:7857–65.
- [67] Hua Y, Omar M, Nolasco-hipolito C, Taufiq-yap YH. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: catalyst characterization and biodiesel yield performance. *Appl Energy* 2015;160:58–70.
- [68] Trakarnpruk W. Biodiesel production from palm fatty acids distillate using tungstophosphoric acid- and Cs-salt immobilized-silica. *Walaialak J Sci Technol* 2012;9:37–47.
- [69] Ardizzone S, Bianchi CL, Cappelletti G, Porta F. Liquid-phase catalytic activity of sulfated zirconia from sol – gel precursors: the role of the surface features. *J Catal* 2004;227:470–8.
- [70] Li Y, Zhang X, Sun L, Zhang J, Xu H. Fatty acid methyl ester synthesis catalyzed by solid superacid catalyst. *Appl Energy* 2010;87:156–9.
- [71] Amani H, Ahmad Z, Asif M, Hameed BH. Transesterification of waste cooking palm oil by MnZr with supported alumina as a potential heterogeneous catalyst. *J Ind Eng Chem* 2014;20:4437–42.
- [72] Weckhuysen BM, Mestl G, Rosynek MP, Krawietz TR, Haw JF, Lunsford JH. Destructive adsorption of carbon tetrachloride on alkaline earth metal oxides. *Phys Chem B* 1998;102:3773–8.
- [73] Correia LM, Saboya RMA, de Sousa Campelo N, Cecilia JA, Rodríguez- Castellón E, Cavalcante Jr CL, Vieira RS. Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sun- flower oil. *Bioresour Technol* 2014;151:207–13.
- [74] Navajas A, Issariyakul T, Arzamendi G, Gandía LM, Dalai AK. Development of eggshell derived catalyst for transesterification of used cooking oil for biodiesel production. *Asia-Pac J Chem Eng* 2013;8:742–8.
- [75] Suryaputra W, Winata I, Indraswati N, Ismadi S. Waste capiz (*Amusium crista-tum*) shell as a new heterogeneous catalyst for biodiesel production. *Renew Energy* 2013;50:795–9.
- [76] Birla A, Singh B, Upadhyay SN, Sharma YC. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresour Technol* 2012;106:95–100.
- [77] Rezaei R, Mohadesi M, Moradi GR. Optimization of biodiesel production using waste mussel shell catalyst. *Fuel* 2013;109:534–41.
- [78] Nakatani N, Takamori H, Takeda K, Sakugawa H. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresour Technol* 2009;100:1510–3.
- [79] Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresour Technol* 2009;100:696–700.
- [80] SL L, YC W, YP T, SY Y. Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO. *Energy Convers Manag* 2015;93:282–8.
- [81] Marinkovi DM, Stankovi MV, Veli AV, Avramovi JM, Miladinovi MR, Stamenkovi OO, et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: current state and perspectives. *Renew Sustain Energy Rev* 2016;56:1387–408.
- [82] Dehkordi AM, Ghasemi M. Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. *Fuel Process Technol* 2012;97:45–51.
- [83] Muhammad Y, Mohd W, Wan A, Aziz ARA. Activity of solid acid catalysts for biodiesel production: a critical review. *Appl Catal A Gen* 2014;470:140–61.
- [84] Rattanaphra D, Harvey A. Simultaneous conversion of triglyceride / free fatty acid mixtures into biodiesel using sulfated zirconia. *Top Catal* 2010;53:773–82.
- [85] Jacobson K, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. *Appl Catal B Environ* 2008;85:86–91.
- [86] Sirisomboonchai S, Abuduwayiti M, Guan G, Samart C, Abliz S, Hao X, et al. Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. *Energy Convers Manag* 2015;95:242–7.
- [87] Alhassan FH, Yunus R, Rashid U, Sirat K, Islam A, Lee HV, et al. Production of biodiesel from mixed waste vegetable oils using ferric hydrogen sulphate as an effective reusable heterogeneous solid acid catalyst. *Appl Catal A Gen* 2013;456:182–7.
- [88] Mansir N, Taufiq-yap YH, Rashid U, Lokman IM. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: a review. *Energy Convers Manag* 2016.
- [89] Lee HV, Juan JC, Tau YH. Preparation and application of binary acid e base  $\text{CaO-La}_2\text{O}_3$  catalyst for biodiesel production. *Renew Energy* 2015;74:124–32.
- [90] Mahesh SE, Ramanathan A, Begum KMMS, Narayanan A. Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst. *Energy Convers Manag* 2015;91:442–50.
- [91] Wong YC, Tan YP, Ramli I, Tee HS. Biodiesel production via transesterification of palm oil by using  $\text{CaO} - \text{CeO}_2$  mixed oxide catalysts. *Fuel* 2015;162:288–93.
- [92] Today C. Transesterification of vegetable oils over CaO catalysts. *Catal Today* 2011;167:64–70.
- [93] Wang H, Wang M, Liu S, Zhao N, Wei W, Sun Y. Influence of preparation methods on the structure and performance of  $\text{CaO} - \text{ZrO}_2$  catalyst for the synthesis of dimethyl carbonate via transesterification. *J Mol Catal A Chem* 2006;258:308–12.
- [94] Shu Q, Jixian G, Nawaz Z, Liao Y, Wang D, Wang J. Synthesis of biodiesel from waste cooking oil with large amounts of free fatty acids using a carbon based solid acid catalyst. *Appl Energy* 2010;87:2589–96.
- [95] Kouzu M, Yamanaka S, Hidaka J, Tsunomori M. Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol. *Appl Catal A Gen* 2009;355:94–9.
- [96] Chen G, Fang B. Preparation of solid acid catalyst from glucose-starch mixture for biodiesel production. *Bioresour Technol* 2011;102:2635–40.
- [97] Avramovi JM, Stamenkovi OS. Biodiesel production by ultrasound-assisted transesterification: state of the art and the perspectives. *Renew Sustain Energy Rev* 2012;16:1193–209.
- [98] Shu Q, Nawaz Z, Gao J, Liao Y, Zhang Q, Wang D, et al. Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: reaction and separation. *Bioresour Technol* 2010;101:5374–84.
- [99] Park Y-M, Lee D, Kim D, Lee J, Lee K. The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. *Catal Today* 2008;131:238–43. <http://dx.doi.org/10.1016/j.cattod.2007.10.052>.
- [100] Harmer MA, Sun Q. Solid acid catalysis using ion-exchange resins. *Appl Catal A Gen* 2001;221:45–62.
- [101] Leung DYC, Guo Y. Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Process Technol* 2006;87:883–90.
- [102] Yujaroen D, Goto M, Sasaki M, Shotipruk A. Esterification of palm fatty reaction, acid distillate (PFAD) in supercritical methanol: effect of hydrolysis on reactivity. *Fuel* 2009;88:2011–6.
- [103] Nakpong P, Woothikanokkhan S. High free fatty acid coconut oil as a potential energy, feedstock for biodiesel production in Thailand. *Renew Energy* 2010;35:1682–7.
- [104] Gole VL, Gogate PR. Intensification of synthesis of biodiesel from non-edible oil using sequential combination of microwave and ultrasound. *Fuel Process Technol* 2013;106:62–9.
- [105] Wan Omar WNN, Amin NAS. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Process Technol* 2011;92:2397–405.
- [106] Guo F, Xiu ZL, Liang ZX. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. *Appl Energy* 2012;98:47–52.
- [107] Nascimento LAS, Angélica RS, da Costa CEF, Zamian JR, Rocha D, Filho GN. Conversion of waste produced by the deodorization of palm oil as feedstock for the production of biodiesel using a catalyst prepared from waste material. *Bioresour Technol* 2011;102:8314–7.