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REVIEW

Catalysts for Biodiesel Production: A Review

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As the world population and modernization increase, energy demand increases. One of the non-sustainable energy sources is fossil fuels. However, fossil fuel consumption raises various environmental and economic issues. Most of the studies focus on sustainable energy sources, which can replace fossil fuel dependence. Biodiesel is an alternative sustainable fuel for diesel power. Biodiesel can produce through the transesterification process. Since the catalyst plays a significant role in the biodiesel yield during a defined reaction time, the addition of a catalyst can increases the reaction rate. This article is outlined the several catalysts used by multiple researchers over the years to increase biodiesel yields.

Keywords: Biodiesel, Catalyst, Esterification, Renewable energy, Transesterification.

INTRODUCTION

Access to energy sources and climate change are two of the biggest challenges facing humanity in this century. The rapidly growing population and increasing prosperity have led to an increase in energy demand. Human civilization is primarily dependent on energy use, which plays a significant role in socio-economic development by improving living standards. Each part of the economy, such as the agricultural industry, commercial, transportation and the domestic sectors, need energy [1]. Fossil fuels are important because they can be burned to produce significant energy. Many aspects of everyday life depend on fuel, especially the transportation of goods and people. The main sources of energy are fossil fuels such as petroleum, coal, and natural gas. Fossil fuels account for 80% of the world's energy needs. Many industries use diesel engines or diesel boilers in the manufacturing process. Automobiles and ships in the transport sector also consume a significant amount of diesel and petrol. This situation leads to a strong dependence on everyday life on fossil fuels [2]. Fossil fuel has a significant environmental impact on global warming and deforestation. Fossil fuels are a limited energy source. Thus, this increasing energy demand has led to the search for alternative renewable fuels such as biodiesel. Biodiesel which is considered clean and environmentally acceptable, can be made from vegetable oils and animal fats [3]. Biodiesel can generate from any fat or oil through a process called transesterification [4].

In transesterification, various types of oils, triglycerides react with alcohols, generally methanol or ethanol, to produce esters and glycerol. A catalyst is added to the reaction to continue the process [5]. Transesterification consists of a sequence of three reversible reactions. The first step is to convert the triglyceride to diglycerides, convert the diglycerides to monoglycerides, and convert the monoglycerides into glycerol, giving each ester molecule for each glyceride. Although the equilibrium leads to the production of fatty acids esters and glycerol, reactions can be reversed. A catalyst is the most important part of the reaction as it is improved the reaction rate and yield. Excess alcohol, which is helping forward reaction, used to shift the equilibrium to the product side, as the reaction is reversible. The reaction can be catalyzed by acid or alkalis or enzymes, and solid metals [6].

The transesterification reaction can proceed with both catalytic and non-catalytic mechanisms. The non-catalytic transesterification mechanism takes place under supercritical conditions. The supercritical method that increases the parasitic energy required for the process requires high temperatures and pressures. For this reason, the catalyst methods are most widely used for biodiesel production at low temperatures and pressures [7]. Therefore, it is essential to study the different catalysts for the production of biodiesel.

Homogeneous catalysts for transesterification: Lorza *et al*. [3] used multi-response surface methodology (MRS) to gain the best combination of input variables used in the transesterification of waste cooking oil (WCO) to improve biodiesel production in the presence of NaOH as a homogeneous catalyst. The optimum condition for a maximum yield of 100% was found to be the molar ratio of 6.52, the catalyst load was 0.78 wt.%, reaction time 19.99 min, reaction speed 499.67rpm, temperature 24.44 ºC, humidity 0.21 wt.% and impurities 0.17 wt.%. Besides, the optimum condition for the maximum heating value was found to be the molar ratio of 6.4, the catalyst load was 1 wt.%, 20min reaction time, reaction rate 499.6 rpm, 33.7 ºC temperature, humidity 0.21 wt.%, and impurities 0.16 wt.%. Under these conditions, the maximum biodiesel yield was 100%.

Ribeiro *et al*. [8] reported that the biodiesel production by using waste cooking oil and bovine tallow as feedstocks. The bio-diesel was produced by alkaline catalyst transesterification and two-step transesterification in cases in which free fatty acids (FFA) content has above 3%. For bovine tallow, 89% of the mass conversion was recorded by one-step transesterification in the presence of 0.5 wt.% of NaOH. In comparison, 85% of the mass conversion was recorded by two steps in the presence of H_2SO_4 0.08 wt.% followed by 0.01 wt.% of NaOH under the same reaction condition of methanol-to-oil molar ratio 6:1, 63 ºC reaction temperature for 2 h reaction time. For waste cooking oil, 92% of the mass conversion was shown in the presence of 0.01 wt.% of NaOH under the same reaction condition. The production of biodiesel from waste vegetable oil using a KM micro mixer reactor was investigated by Elkady *et al.* [9] through pre-treatment and transesterification process in the presence of methanol. The parameters affecting the biodiesel production process, such as alcohol-to-oil molar ratio, catalyst concentration, tetrahydrofuran covalent and the volum-etric flow rate of the input fluid, were optimized. A maximum biodiesel production yield of 97% was reported using an oil molar ratio of 12:1 methanol-to-oil in the presence of 1 wt.% NaOH, 70 ºC of reaction temperature and THF to methanol volume ratio of 0.3:1 (v/v) at 60 mL/h flow rate.

Raja *et al*. [10] reported the viscosity of Jatropha oil was decreased significantly after transesterification and was being compared to that of diesel under the best combination of parameters was a 6:1 molar ratio of methanol-to-oil, 0.92 wt.% NaOH catalyst, 60 ºC reaction temperature and 60 min reaction time. In this study, the biodiesel effects of various parameters such as temperature, time, reactivity rate and catalytic concentration on biodiesel yield were analyzed. Soon *et al*. [11] investigated the use of an ultrasound clamp for biodiesel production from vegetable oil. Based on the result obtained, the highest fatty acid methyl ester (FAME) yield was 96% using the ultrasound clamp of the tube reactor, with an oil-to-methanol molar ratio of 9: 1 and a catalyst (NaOH) concentration of 0.75 wt.% at 64 ºC. Banerjee *et al*. [12] have been conducted a study on the production of biodiesel from used vegetable oils. The reaction was carried out under reflection at 55 ºC for 90 min. The reaction speed was maintained at 1000 rpm and the NaOH concentration was 0.69 wt.%.The test was performed to identify the best ratio to obtain the highest biodiesel yield by changing the oil-to-methanol ratio (1: 3, 1: 6, 1:12, 1:15). The amount of catalyst used, the reaction temperature and the reaction speed were kept constant. A maximum yield of 94% was obtained using a more significant amount of methanol. Therefore, the optimal molar ratio was 1:15.

Dhanke *et al*. [13] conducted a study on the transmission of cotton oil in an ultrasonic cavity reactor. The molecular ratio of oil-to-alcohol varied from 1:6 to 1:15, the catalyst of NaOH concentration was altered from 0.5 to 2 wt.%, the reaction temperature varied from 30 ºC to 60 ºC and the reaction time was varied from 10 to 40 min. The best condition for the production of biodiesel from cotton oil to obtain minimum kinematic viscosity (4cSt) was a 1:9 molar ratio, 1 wt.% NaOH at 50 ºC reaction temperature at 30 min reaction time. Shahid *et al*. [14] investigated the effect of the cooking oil methyl ester used on the compression engine. In this study, cooking oil was transesterified using 1%(w/v) NaOH and 20% methanol in a temperature range of 65-69ºC under the reaction time of 2 h and that resulted in conversion efficiency is 92.5% (v/v).

Rashid *et al*. [15] conducted a study on optimizing the alkaline transesterification of rice bran oil for biodiesel production with the response surface methodology (RSM). Experiments were carried out by altering each parameter as follows, the molar ratio of methanol to oil was 3:1-12:1, $NaOCH_3$ as the catalyst concentration was 0.5-1.25 wt.%, the reaction temperature was 45-65 ºC, and the reaction time was 30-90 min. The reaction conditions for the transesterification of rice bran oil were 7.5:1 molar ratio methanol-to-oil, 0.88wt.% $NaOCH_3$ concentration, 55 ºC reaction temperature and 60 min reaction time. Rice bran oil methyl esters were 83.3% under optimum reaction conditions.

Chen *et al*. [16] enhanced the yield of biodiesel fields from waste cooking oil using $NaOCH_3$ rather than NaOH and a microwave heating system. The article emphasized that biodiesel's yield was increased with the increase of catalyst content from 0.50 wt.% to 0.75 wt.% and the yield was decreased when the catalyst concentration increased from 0.75 wt.% to 1.50 wt.%. The best performance was 0.75 wt.% NaOH and 0.75 wt.% CH_3ONa for waste cooking oil. The yields of biodiesel under the $NaOCH_3$ catalyst were higher than those under the NaOH catalyst. Although an excess catalyst can increase biodiesel yields, glycerin was increased to reduce biodiesel yields due to saponification. The best performance was obtained with 0.75 wt.% NaOH and 0.75 wt.% $NaOCH_3$ catalysts, respectively. The maximum yield of biodiesel made from waste cooking oil under conventional heating (65 ºC) was 96.6% in 90 min and the maximum yield of biodiesel made from waste cooking oil was 97.9% in 3 min. The author, therefore, concluded the optimum reaction conditions were 0.75 wt.% $NaOCH_3$ catalyst, 6:1 molar ratio of methanol-to-oil, 3 min of reaction time and 750 W of microwave power.

Canakci & Gerpen [17] investigated the use of low-cost, high-FFA feedstock such as brown grease to produce fuel-quality biodiesel through two-stage esterification, followed by a transesterification reaction in the presence of H_2SO_4 and NaOH catalysts, respectively. In first stage, the acid value was reduced from 66.08 to 5.15 mg KOH/g by an esterification reaction with H_2SO_4 5 wt.% under reaction condition of 20:1 methanol-to-oil molar ratio, 60 ºC, 1 h reaction time. Subsequently, further esterification was performed to further reduce the acid value from 5.15 to 2.03 mg KOH/g at the same reaction time and reaction temperature with H_2SO_4 10 wt.% and 40:1 molar ratio. Then, at 60 ºC, $NaOCH_3$ was used as a base catalyst to performed transesterification using 0.21 wt.% catalyst, at a molar ratio of 6:1 and yielded 75.12% biodiesel as a resultant.

Patel *et al*. [18] investigated the design and development of a small-scale biodiesel production unit using $NaOCH_3$ as a catalyst to understand its catalytic activity in the transesterification of *Leptadenia reticulata* oil. This esterification was performed to reduce the FFA content of *Leptadenia reticulata* oil, which was identified as 34.8 mg KOH/g. The esterification process was carried out with 1 wt.% H_2SO_4 acid, methanol in an oil volume ratio of 0.45:1. The whole reaction mixture was stirred vigorously at 600 rpm for 2 h under reflux conditions at 60 ºC. The *Leptadenia reticulata* methyl ester yield as a result of the optimum reaction was 78%, which was the optimum value of the process parameters for the FFA transmission of *Leptadenia reticulata* oil, under the reaction condition of methanol-to-oil molar ratio of 6:1, the $NaOCH_3$ concentration was 1.5 wt.%, reaction time 180 min and the reaction temperature was 60 ºC.

Dupas *et al*. [19] investigated the best reaction time for biodiesel production from waste cooking oil that had the initial acid value of 6.1721mg KOH/g. The transesterification process was performed by mixing KOH 1 wt.% with a methanol-to-oil molar ratio of 6:1 at 65 ºC. With time variations of 30, 45, 60, 75 and 90 min. Based on the characteristic of biodiesel, density 0.886 g L^{-1}, the viscosity of 5.89 cSt and acid value of 0.256 mg KOH/g were obtained for 90, 75 and 60 min, respectively. Moreover, Bouaid *et al*. [20] conducted the statistical experiments to study the effect of temperature and catalyst concentration on the yield and purity of biodiesel obtained from used frying oil with different FFA content (0-4%). According to the study, the maximum yield and purity for the oil with 4% FFA was recorded as 98.45% (purity 99%) under reaction conditions at 30 ºC, KOH 0.8wt.%, the methanol-to-oil molar ratio of 6:1 and 600 rpm.

Bakir & Fadhil [21] converted chicken fried oil into various biodiesels by single-step transesterification and two-step transesterification, namely acid-base and base-base catalyst transesterification. Single-step transesterification was conducted using a freshly prepared KOH 0.50 wt.% with the methanol to oil molar ratio of 6:1 at 60 ºC for 1 h. The maximum yield of 87.40% was obtained. Two-step base-base catalyst transesterification was performed by repeating the single-step transesterification twice and yielding 92%. Acid-base catalyst transesterification was carried out at a ratio of 1 wt.% HCl, 6:1 of molar ratio at 60 ºC for 1 h followed by KOH 0.8 wt.% under the same reaction condition that was given a yield of 90%. Kachhwaha & Pal [22] presented a comparative information on the biodiesel production process using low-frequency ultrasonic power (28-33 kHz) and the conventional mechanical excitation method. For this purpose, waste cooking oil and *Citrullus colocyntis* (Tumba) oil were used as biodiesel feedstock. Experiments were performed with methanol to oil molar ratios of 6:1 and 4.5:1 with three different catalyst percentages (0.5, 0.75 and 1%) of KOH. The temperature of the mixture was kept between 40-55 ºC during the reaction. For tumba, the maximum bio-diesel yield of the ultrasonic method was 92.8% under the reaction condition of 0.5 wt% KOH with a 6:1 molar ratio in 20 min. The maximum yield for waste cooking oil from the ultrasonic method was 95.2%, which was obtained in 21 min at a ratio of 4.5: 1 for 0.5% KOH.

Harabi *et al*. [23] explored the optimization of homogeneous transesterification of waste frying oil with 0.63 mg KOH/g of acid value to biodiesel through KOH catalyst. In this regard, the response surface methodology (RSM) for determining the relationship between the ratio of methanol and waste frying oil molar (3:1-12:1), KOH concentration (0.5-2%) and temperature (25-65 ºC) were applied. The transesterification of waste frying oil produced optimal methanol to an oil molar ratio of 7.3:1. The reaction temperature was 58.30 ºC with a KOH load of 0.5 wt.% producing a maximum methyl ester yield of 96.33%. Abbaszadeh *et al*. [24] investigated the effective parameters on biodiesel purification through the wet washing process to produce biodiesel from waste cooking oil using KOH 1 wt.%. The reaction was carried out at 60 ºC for 2 h at a mixture speed of 300 rpm in a volumetric ratio of 1:4 alcohol and oil in a pressurized environment.

Kawentar & Budiman [25] converted the second-used cooking oil into biodiesel under the optimum condition of its process. This research was conducted using KOH as a base catalyst. In this study, it was found that the kinetic reaction of transesteri-fication of second-used cooking oil can be expressed by $k = 0.0251\exp^{(-15.29/RT)}$ $dm^3/(mol\ min)$. The optimum condition with ester content was obtained at 92.76% of biodiesel production at 66.5 ºC and the molecular ratio of methanol to oil was 6.18:1 and 1 wt.% KOH. Fadhil *et al*. [26] prepared biodiesel fuels from a spent fish frying oil through two-step transesterification in the presence of the acid-base catalyst. The oil was initially pre-treated with 1.0 wt.% HCl and methanol to reduce the initial acid value of 5.41 mg KOH/g. The study was revealed that oil 0.50 wt.% KOH, 6:1 oil molar ratio of methanol-to-oil, the reaction temperature was 60 ºC, the reaction speed was 600 rpm and the 1 h was optimal as they were yielded high biodiesel yields of 94%. The esterification reaction was performed at the same reaction time, speed, temperature and molar ratio.

Heterogeneous catalysts for transesterification: Encinar *et al*. [27] conducted experiments with various co-solvents to analyze the impact of biodiesel production from rapeseed oil. The study was conducted concurrently using KOH, $Ba(OH)_2$, LiOH, *p*-TSA, $ZnCl_2$, $AlCl_3$ and BF_3 catalysts. The reaction results were showed that acid catalysts such as *p*-TSA, $ZnCl_2$, $AlCl_3$ and BF_3 were not produced biodiesel under the reaction conditions, with a molar ratio of methanol-to-oil 9:1, a molar ratio of methanol-to-diethyl ether 1:1, a reaction temperature of 303 K, 700 rpm and 120 min of reaction. However, when 0.7wt.% KOH was used as a catalyst, it was yielded 97.6%

biodiesel under the same reaction condition, the 0.7 wt.% $Ba(OH)_2$ catalyst was produced the highest biodiesel yield of 98.3% and 0.7 wt.% LiOH was produced at 96.8% under that same reaction condition, but the obtained biodiesel viscosity from $Ba(OH)_2$ and LiOH were had lower viscosity and higher water content than EN-14214 specifications, respectively.

Hasanudin & Rachmat [28] synthesized an acid catalyst of WO_3-ZrO_2 prepared from a combination of tungsten and zirconium oxide and evaluated biodiesel production from low-quality oil Palm Oil Mill Effluent (POME) sludge in the presence of WO_3-ZrO_2 as the catalyst. Tungsten and zirconium oxide composite were indicated that increasing the amount of catalyst used for conversion would increase biodiesel production. The optimum value was reached 10 wt.% WO_3-ZrO_2, 8:1 methanol-to-oil molar ratio, the reaction temperature was 70 ºC for a reaction time of 2 h and it was converted 74.88% of the oil into biodiesel. Patil *et al*. [29] studied H_2SO_4 (two-step) and microwave-assisted transesterification (one-step) using BaO and KOH to evaluate the efficiency of microwave processing of biodiesel production from WCO 17.41 mg KOH/g of acid value. Based on the results, the esterification process was carried out to reduce the FFA content of the waste cooking oil in the presence of H_2SO_4 0.5 wt.%, 9:1 methanol-to-oil molar ratio. The transesterification process was carried out using KOH 2 wt.% at 80 ºC for 105 min, which facilitated 92% of the free fatty methyl ester. Moreover, KOH and BaO were used to obtain a maximum yield of 92% and 96%, respectively by microwave-assisted transmission. Both reactions were performed under the same catalyst concentration of 2 wt.% with the same reaction time of 6 min. The molar ratio from methanol-to-oil in KOH and BaO was kept as 9:1 and 12:1, respectively.

Wang *et al*. [30] investigated a two-step catalytic process for the preparation of biodiesel from WCO with an acid value of 75.92 ± 0.036 mg KOH /g. The FFA of WCO were esterified with $Fe_2(SO_4)_3$ and methanol in the first step. The triglyceride in WCO was transistorized with methanol catalyzed by KOH. When 2 wt.% of $Fe_2(SO_4)_3$ was added to the methanol containing reaction system in a 10:1 molar ratio composition, the conversion ratio of FFA reached 97.22% and reacted at 95 ºC for 4 h. The transesterification of the remaining triglycerides in a reaction system containing KOH 1 wt.% and methanol oil: 6:1 molar ratio was carried out for 1 h at 65ºC. The final product containing 97.02% of the biodiesel obtained after the two-step catalytic process was analyzed by gas chromatography.

Javidialesaadi & Raeissi [31] examined the effect of pretreatment on biodiesel production from acid oil that contained a high FFA level, such as 44.5%. Methanol-to-oil ratio (0.2 to 1.2 v/v), H_2SO_4 (0.5 to 6 v/v %) and reaction time (20 to 120 min) were studied to observe the progress of the reaction. The highest conversion was observed when H_2SO_4 was 3 v/v % at 50 ºC and the methanol to oil was 80 v/v% at 1h reaction time.

Saifuddin & Boyce [32] studied the kinetics of esterification of free fatty acids (FFA) in sunflower oil with methanol in the presence of H_2SO_4 at concentrations of 5 and 10 wt.%. The experimental results showed that the first reaction was consistent with the first-order kinetic law and the second sequence with the reverse reaction. As the catalyst concentration increased, the activation energy decreased from 50745 to 44559 J mol^{-1} for the next reaction. This study also revealed that the reaction rate increased as H_2SO_4 concentration increased from 5 wt.% to 10 wt.%. However, the increase was negligible. Therefore, as the optimum reaction state, the molecular ratio of methanol to the oil of 60:1.5wt.% H_2SO_4 at 60 ºC led to the final acid value for oils below 1 mg KOH / g for 120 min. Chen *et al*. [33] studied the optimum catalyst concentration of xSO_4^{2-}/TiO_2 for the highest conversion of *Jatropha curcas* L. seed oil. The $0.5SO_4^{2-}/TiO_2$, $1.0SO_4^{2-}/TiO_2$, $1.5SO_4^{2-}/TiO_2$ and $2.0SO_4^{2-}/TiO_2$ were prepared by the impregnation with 0.5M H_2SO_4, 1.0M H_2SO_4, 1.5 M H_2SO_4 and 2.0M H_2SO_4, respectively. The highest conversion of 85% was recorded for $1.5SO_4^{2-}/TiO_2$ at the methanol-to-oil molar ratio of 9:1 with catalyst weight of 4 wt.%, for a reaction time of 24 h and the stirring rate of 600 rpm. xSO_4^{2-}/TiO_2 exhibited the higher catalytic activity than TiO_2, and the surface area increases with the sulfuric acid content because of the impregnation.

Widayat *et al*. [34] produced the biodiesel using a heterogeneous catalyst CaO that derived from limestone, $Ca(OH)_2$ and $CaCO_3$, with the calcination process at 900 ºC for 1/2 h. Based on the CaO composition, the limestone CaO was showed a higher performance than $Ca(OH)_2$ and $CaCO_3$. The transesterification was performed for vegetable oil, the catalyst load was 2.6 wt.%, the reaction time of 40 min and the molar ratio was 9:1. In this study, CaO from limestone was yielded 89.98% of FAME, whereas CaO from $Ca(OH)_2$ and CaO from $CaCO_3$ yielded 85.15% and 78.71%, respectively. Qin *et al*. [35] used the modified CaO by ethyl bromoacetate for biodiesel production. The study showed that the biodiesel production increased from 66.2% to 96.5% under using 10 wt.% modified CaO than commercial CaO at 65 ºC for a reaction time of 4 h, the molar ratio of methanol-to-rapeseed oil was 15:1 and the modifier loading of 0.2%. Moreover, this study confirmed that the modified CaO showed good stability in a high-water content reaction system due to a hydrophilic protective layer formed over the CaO surface after modification. Thus, water diffusion on the CaO surface can be effectively prevented.

Peng *et al*. [36] provided an evidence that the application of a microwave heating system for biodiesel production. The best performance for biodiesel production from waste cooking oil was recorded at 5 wt.% waste eggshell catalyst. The CaO was derived from the calcination of waste eggshell exhibits a high catalytic performance for biodiesel production from the transesterification reactions of methanol and the waste cooking oil. The primary results of this study were observed with a significant reaction time of 120 min to 165 min, which resulted in a significant increase in biodiesel yield. However, a further increase of 10 min decreases the FAME yield due to the increase of glycerin solubility. The oil molar ratio from methanol to oil of 7:1 to 9:1 resulted in a significant increase in biodiesel yield, which subsequently decreased with an 11:1 ratio. There is also strong evidence that rising temperatures from 45 ºC to 65 ºC improved the biodiesel production. Later, as the temperature rose to 85ºC, it was dropped. Therefore, it was concluded that the optimum reaction conditions under this study were 5 wt.% CaO, 9:1 methanol to oil molar ratio and a reaction time of

165 min at 85 ºC, which facilitated up to 87.8% FAME yield. Moradi *et al*. [37] studied CaO and MgO as a heterogeneous catalyst for biodiesel production from waste cooking oil. Waste mussel shells and demineralized water treatment precipitates as sources of $CaCO_3$ and $MgCO_3$ were converted to CaO and MgO at < 900 ºC. The methanol-to-oil was reacted at a molar ratio of 24:1 and 22.5:1 in the presence of 12 wt.% and 9.08 wt.% of mussel shell-based and demineralized water treatment precipitates based catalysts, respectively. Accordingly, the demineralized water treatment catalyst had a maximum conversion yield of 84%, while the waste mussel shells were yielded 83% under 348 K and 8 h reaction time.

Salamatinia *et al*. [38] performed the transesterification of palm oil applying MgO, BaO, CaO and SrO as catalysts. MgO did not acts as a good catalytic activity and CaO offered unsuitable products over a long reaction time. BaO showed the best biodiesel yield up to 95%, while SrO yielded 91%. The molar ratio of methanol-to-oil of 9:1, reaction temperature at 60 ºC, reaction time 180 min and 5% of catalyst loading were found to be optimal reaction conditions. When catalysts were reused, the basicity of BaO decreased and the basicity of SrO and CaO remained constant. Mootabadi *et al*. [39] studied the ultrasonic transesterification of palm oil in the presence of alkaline earth metal oxide catalysts such as CaO, SrO and BaO. According to the basic strength, the catalytic activity increased as the basic strength increased in the order: CaO < SrO < BaO. When using ultrasonic method, the yield obtained in 60 min was increased from 5.5% to 77.3% for CaO, from 48.2% to 95.2% for SrO and from 67.3% to 95.2% for BaO. The optimum amplitude for transesterification of palm oil was 50%. In the presence of ultrasonic energy, the optimal methanol-to-oil ratio was 12:1 for the CaO catalyst and 9:1 for the BaO and SrO. The concentration of the catalyst was 3 wt.%. Despite the high activity, BaO catalyst, especially under ultrasonic conditions, underwent a more severe activity drop than the catalyst reuse test. Catalyst dissolution was found to be primarily responsible for the decrease in reactivity of reusable catalysts.

Wendi *et al*. [40] also studied the production of biodiesel using CaO as an catalyst from waste beef tallow. By calcinating at 900 ºC for 2 h, the industrial waste eggshell was converted into the CaO. The high FFA content of the oil was reduced from 1.86% to 0.35% in the presence of 0.5 wt.% H_2SO_4 by acid catalyst esterification at 60 ºC for 4 h reaction time with a 6:1 molar ratio of menthol-to-oil. Under the best transesterification reaction conditions, the maximum yield of beef methyl ester was 82.43% obtained using a 9:1 molar ratio at 55 ºC and 3 wt.% of CaO catalyst within 1.5 h. Omar *et al*. [41] studied the relationship between the reaction temperature, the reaction time and the molar ratio of methanol to oil in the pre-treatment step. The acid-catalyzing esterification process was performed with 30.4 wt.% $Fe_2(SO_4)$ to reduce the FFA content, and the waste cooking oil with 32% of the FFA was used as a feedstock in the esterification reaction. Central composite design (CCD) and RSM were used to determine the best-operating conditions for the pre-treatment steps. The optimum conditions for the reaction temperature, the reaction time and the methanol-to-oil molar ratio were 60 ºC, 3 h and 7:1, respectively. Moreover, the transesterification was conducted with 0.5 wt.% CaO under the same optimum reaction conditions to obtain the maximum FAME which was 81.3%.

Soares Dias *et al*. [42] investigated CaO as a catalyst for converting waste frying oil to biodiesel. Under the acid value of the oil was 7.32 mg KOH/g, the highest yield of 87% was obtained at 60 ºC with a catalyst content of 5 wt.% and methanol-to-oil molar ratio in a 12:1 at a reaction time of 4 h. The study was reported that the oil with high acidity values (> 20 mgKOH /g) could be led the catalyst to become amorphous and inactive. Therefore, as the acidity of the oil increases, so does the amount of soap make. Kouzu *et al*. [43] studied the conversion of edible soybean oil (acid value less than 0.1 mg KOH/g) with CaO, $Ca(OH)_2$ or $CaCO_3$ to study a basic catalyst for biodiesel production. At 1 h of reaction time and the molar ratio of methanol to vegetable oil was close to 12, the yield of FAME was 93% for CaO, 12% for $Ca(OH)_2$ and 0% for $CaCO_3$. Under the same reaction conditions, MgO was not significantly active during transesterification. But NaOH was converted to complete FAME with homogeneous catalysis. Furthermore, CaO was used for further tests on the transesterification of WCO with an acid value of 5.1 mg KOH/g. At 2 h of reaction time, the yield of FAME was more than 99%, but by reacting with the free fatty acids was added in the WCO during the initial stage of transesterification, where part of the catalyst was converted to soap. The calcium concentration in FAME increased from 187 ppm to 3065 ppm due to the neutral reaction of the catalyst. Only free fatty acids can be converted to FAME by processing when refluxing WCO with methanol when cation exchange resin is present. WCO with an acid value of 0.3 mg KOH/g resulted in the production of FAME including 565 ppm calcium.

Liu *et al*. [44] synthesized $Ca(OCH_2CH_3)_2$ as catalyst for the transesterification of soya bean oil with methanol and ethanol to biodiesel. Experimental outcomes revealed that 95% of biodiesel was yielded within 1.5 h under the optimal conditions of methanol-to-oil in a molar ratio of 12:1 with 3 wt.% $Ca(OCH_2CH_3)_2$ catalyst at 65 ºC. It has also been shown that the catalytic activity of $Ca(OCH_2CH_3)_2$ was better than that of CaO. In addition, when soybean oil was catalyzed into biodiesel with ethanol, a yield of 91.8% was obtained. Chen *et al*. [45] used alkaline earth metal oxides MgO, CaO and SrO as catalysts for the transesterification of olive oil with methanol. The most efficient catalyst was further doped with CaO or SiO_2 to enhance its catalytic activity, which was evaluated by transesterification at different reaction temperatures, using different water contents and different oil types. results were shown SrO the conversion of refined olive oil into biodiesel in 15 min was more than 80% and the catalytic activity of CaO and MgO was found to be very low during transesterification at 65 ºC, 600 rpm, the molar ratio of the oil-to-methanol of 1: 6 and catalyst loading 5wt.%. Although the reaction was extended to 3 h, only 15.1% and 0% conversions were detected, respectively, when CaO and MgO were used as catalysts, respectively. Using SrO doped SiO_2 (SrO/SiO_2) further increased the conversion to 95% in 10 min. The SrO/SiO_2 also showed good water and FFA tolerance, when the water and FFA content was increased to 3.23 and 3.14 wt.%, respectively, the conversion was still greater than 90% in 20 min. The addition of hexane significantly increased the reuse of SrO/SiO_2 for transesterification and the biodiesel production was still close to 80%.

Liu *et al*. [46] studied the transesterification of soybean oil to biodiesel using SrO as a base catalyst. The SrO exhibited excellent catalytic activity and stability due to its strong basicity and long catalyst life and insoluble in methanol. When soybean oil was transesterified to biodiesel, the biodiesel yield was exceeded 95% in 30 min. The SrO also provides a higher catalytic activity than homogenous catalysts. The optimum conditions for the best economic results were methanol-to-oil with a 12:1 molar ratio and a 3 wt.% SrO catalyst at 65 ºC. Moreover, the study was elaborated under mild temperature and pressure conditions, the reaction was completed in a short time. As a base catalyst, SrO reduces biodiesel production costs and has the potential for industrial applications in the transesterification of vegetable oil to biodiesel. Roschat *et al*. [47] used SrO as a solid catalyst for the simple conversion of palm oil into biodiesel production *via* the ethanolysis reaction. The reaction results showed that the optimized parameters were catalyst load: 5 wt.%, the ethanol-to-oil molar ratio as 12: 1 and the reaction temperature was 80 ºC. A fatty acid ethyl ester (FAEE or biodiesel) yield of 98.2% can be obtained in 3 h and also the SrO catalyst was reused at least 5 times with excellent catalytic activity without regeneration or treatment.

Suwannasom *et al*. [48] studied the relationship between the biodiesel production parameters from waste cooking oil using bovine waste bone as a catalyst for high conversion of fatty acids to methyl esters. The effect of three independent variables was used as the optimal condition using the RSM to maximize biodiesel yield percentage. The optimum values of the variables were the methanol-to-oil molar ratio of 15.49: 1, catalyst load of 6.42 wt.%, and the reaction time was 128.67 min. Under the optimal conditions, the biodiesel percentage reached 97.59%. Peng *et al*. [49] studied an acid catalyst consisting of SO_4^{2-}/TiO_2-SiO_2 for its activation to produce biodiesel from several low-cost feedstocks of components with high FFA. The effect of the reaction parameters was also investigated and the optimum reaction parameters were achieved at 200 ºC, at a molar ratio of methanol-to-oil 9: 1 having a catalyst concentration of 3 wt.%. for 50% oleic acid + 50% refined cottonseed oil. As the catalyst concentration increased from 1 to 3 wt.%, the yield of methyl ester was increased significantly from 84% to 92%. However, when the catalyst concentration was further increased to 5 wt.%, the reaction rate and methyl ester yield were increased slightly.

Garcia *et al*. [50] synthesized sulfated zirconia (S-ZrO_2) by solvent free method and utilized in the transesterification of refined soybean oil with a free fatty acid content of 0.086 ± 0.001 mg KOH/g. Under the optimum conditions (an oil-to-alcohol molar ratio of 1:20, 120 ºC, 1 h and 5 wt.% catalysts), the alcohol conversion of soybean oil was 98.6% (methanolysis) and 92% (ethanolysis), respectively. After 2 h, the oleic acid esterification with methanol was completed and the 8.5% of conversion was recorded for zirconia sulfated by the standard method with low activity, while conventional zirconia was inactive for methanolysis under the conditions optimized for S-ZrO_2. Muthu *et al*. [51] also synthesized sulfated zirconia (SZ) by a solvent-free method and used to produce neem methyl ester formulated by a two-step process from neem oil with methanol in the presence of a catalyst. An acid catalyst (SZ) was employed for esterification while an alkali (KOH) as catalyst was employed for the transesterification reaction. High FFA level (24.76mg KOH/g oil) of crude neem oil was reduced to less than 2 mg KOH/g by an acid-catalyst pre-treatment process of esterification using SZ a with a molar ratio of methanol-to-oil 9: 1 at 65 ºC in 2 h, whereas transesterification with 1% wt. of KOH facilitated 95% of biodiesel.

Jitputti *et al*. [52] reported the preliminary results using some acidic and basic solids such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, $SO4_4^{2-}/ZrO_2$, KNO_3/KL zeolite and KNO_3/ZrO_2 as heterogeneous catalysts for crude palm kernel oil and crude coconut oil transesterification with methanol. The experiments were performed at a methanol-to-oil molar ratio of 6:1, using a 3 wt.% of the catalyst, at 50 bars under N_2 atmosphere, the temperature at 200 ºC and the 350 rpm stirrer. Based on the methyl ester yield, the SO_4^{2-}/ZrO_2 acid catalyst gives the highest yield compared to other solid catalysts. The activity of catalysts for crude palm kernel oil transesterification was $SO_4^{2-}/ZrO_2 > SO_4^{2-}/SnO2 > ZnO > KNO_3/ZrO_2 > KNO_3$/KL zeolite > ZrO_2. In the case of crude coconut oil, the activity was $SO_4^{2-}/ZrO_2 > SO_4^{2-}/SnO_2 > ZnO > KNO_3$/KL zeolite > $KNO_3/ZrO_2 > ZrO_2$. The SO_4^{2-}/ ZrO_2 was yielded 90.3% of methyl esters from crude palm kernel oil and 86.3% from crude oil.

Lam *et al*. [53] utilized sulfated tin oxide as a solid superacid catalyst for biodiesel production. The superacid sulfated tin oxide catalyst (SO_4^{2-}/SnO_2) was prepared using an impregnation method for the biodiesel production through a heterogeneous transesterification process. The bimetallic effect of catalyst was also studied in which SnO_2 was mixed with SiO_2 and Al_2O_3 at different weight ratios, respectively, to enhance the catalytic activity of SnO_2. The BET surface area of SO_4^{2-}/SnO_2 was lower than the unsulfated SnO_2 and the optimum yield of 92.3% was obtained at 150 ºC consisted of SO_4^{2-}/SnO_2-SiO_2 catalyst loading 3 wt.%, the molar ratio of methanol-to-oil of 15:1 and the reaction time of 3 h. Pereira *et al*. [54] demonstrated the application of $SnSO_4$ catalyst for the esterification of oleic acid and acid soybean oil with a high content of FFA. The feedstock that contained 70 wt.% of FFA (oleic acid), the highest biodiesel yield of 92%, was obtained at 100 ºC under automatic pressure for 3 h of reaction time with 5 wt.% $SnSO_4$ and the ethanol-to-oil molar ratio of 3.5:1. Akbar *et al*. [55] prepared Na/SiO_2 as a solid catalyst by sol-gel method for the transesterification of jatropha oil with methanol to produce a fatty acid methyl ester. Excellent catalytic activity for Na/SiO_2 was demonstrated with a molar ratio of 50:50 of Na-to-Si calcinated at 600 ºC, which resulted in the vegetable oil conversion of 99%. The optimum reaction conditions were achieved at 65 ºC with an oil-to-methanol molar ratio of 1:15 and 6 wt.% of catalyst. The catalyst exhibited the high activity under mild conditions and a relatively short reaction time of 45 min.

Silva *et al*. [56] reported Cu(II) and Co(II) impregnated on chitosan catalysts for FAME synthesis from soybean oil and babassu oil. The experiment was performed using the methanol-to-oil weight ratio of 1: 5 at the catalyst concentration of 2 wt.% and the mixture was agitated at 70 ºC for 3 h at pH 8.5. The organic phase was separated by centrifugation and dried using anhydrous sodium sulfate. Biodiesel yield from soybean oil using Co(II) was 94.01% and from Cu(II) was 88.82%. In case of babassu oil, the yield from using Co(II) was 86.65%, whereas using Cu(II) impregnated on chitosan catalysts, the obtained yield was 71.89%. Therefore, it has been concluded that the conversion of oil into biodiesel was better when using chitosan Co(II) adsorbed. Baskar *et al.* [57] synthesized and utilized Mn-doped-ZnO as a heterogeneous catalyst for the production of biodiesel from mahua oil. It was found that 8% (w/v) catalyst concentration, 1:7 (v/v) oil-to-methanol ratio, 50 min reaction time and 50 ºC maximum reaction temperature were the optimal operating conditions for biodiesel which yielded 97%. Nakagaki *et al.* [58] synthesized sodium molybdate as heterogeneous catalyst for the methanolysis of various renewable lipid sources derived from soybean oil. Molar ratios of methanol-to-oil at 21:1-60:1 were evaluated at a catalyst concentration of 0.5-10.0% and at 0.5-3 h reaction time. The investigation was done for other ingredients such as degummed soybean oil and used frying oil. When the catalyst concentration was increased from 1.0 to 2.0 wt.%, the conversion to methyl ester was increased from 11.9 to 80.4 wt.%. The maximum reaction yield (95.6%) was obtained at a catalyst concentration of 5 wt.% under the optimum reaction condition was obtained at 120 ºC, methanol-to-oil molar ratio of 54:1 for a reaction time of 180 min. The molybdenum(VI) complex has a high Lewis acidity and thus, the catalyst was easily recovered and recyclable for another catalyst reaction with similar activity after washing.

Xie *et al.* [59] synthesized KOH based NaX zeolites as a heterogeneous based catalyst for the transesterification of soybean oil to methyl ester with methanol. A catalyst loaded with 10% KOH followed by heating at 393 K for 3 h provides the best result with an 85.6% yield under the optimized reaction conditions. The influence of loading amount of KOH on the conversion was recognized under the reaction conditions of methanol-to-oil molar ratio 10:1, catalyst amount 3 wt.%, reaction time 8 h and the reaction temperature of 338 K. It was notified that the loading of KOH on NaX zeolite resulted in the higher basic strength than the parent NaX zeolite. After loading with KOH, the porous structure of the zeolite required for catalysis can be retained. Ramos *et al.* [60] studied three zeolites, such as Mordenite, beta and X, to convert sunflower oil into biodiesel. The effect of various loaded metals on such zeolites was examined. Experiment was conducted for 7 h at atmospheric pressure, the catalyst loading 10wt.%, methanol-to-oil molar ratio of 6:1, reaction temperature of 60 ºC and stirring rate of 500 rpm. The authors claimed that the incorporation of sodium increased the base strength and number of base sites of parent zeolite (NaX) and increased the catalytic activity for the production of methyl ester. Therefore, the incorporated Na content increased to 0.1, 1 and 3, resulted in the the increased yields of methyl esters to 5.3%, 38.4% and 95.1%, respectively. Compared to other zeolites such as modernite and beta, zeolite X has higher activity because of having a higher concentration of super-base sites than the other two zeolites. However, when zeolite X was combined with sodium bentonite as a binder, the catalyst activity was similar.

Wu *et al.* [61] investigated the transesterification of soybean oil to biodiesel using zeolite (NaY, KL and NaZSM-5) supported CaO as strong base catalysts. The study revealed that the CaO catalyst activity increased when supported with zeolite and CaO/NaY, which exhibit the best performance due to the highest surface area of NaY zeolite. The activity order of the catalyst was as follows; CaO/NaY > CaO/KL > CaO/NaZSM-5 > CaO. Factors affecting biodiesel yield were investigated to optimize the reaction conditions. 95% biodiesel yield using CaO/NaY (30 wt.% of CaO loading on NaY zeolite), methanol-to-oil molar ratio 9:1, reaction temperature 65 ºC, reaction time 3 h and catalyst 3 wt.%. The results showed that the supported catalyst has the capacity for water resistance and acid resistance. Higher yields (< 80%) can be obtained, when the acid value and water content of the oil are less than 4 mg KOH/g and 1.5%, respectively. Feyzi & Khajavi [62] investigated the activity of strontium nanocatalysts, which support ZSM-5 zeolite in the transesterification of sunflower oil to produce biodiesel FAME. Catalysts were prepared by the incipient wetness impregnation method. Effect of Sr/ZSM-5 mass ratio on catalyst activity was tested under reaction conditions of the methanol-to-oil molar ratio of 12:1, reaction temperature of 60 ºC, stirring rate of 500 rpm, and reaction time of 240 min. The catalyst with 6 wt.% Sr/ZSM-5 was exhibited as the best catalyst performance for biodiesel production and reached 80.9 % of biodiesel yield. The effect of barium load on the catalytic activity under the same reaction conditions was examined and showed that 4% barium as the best catalyst performance compared to the other catalysts tested. Therefore, the transesterification reaction of sunflower oil with methanol-to-oil 9:1 molar ratio. The reaction temperature of 60 ºC and the mechanical reaction at 500 rpm with a reaction time of 180 min. Yields a maximum of 87.7% biodiesel in the presence of yBa – xSr/ZSM-5 (x = 6 wt.% Sr based on ZSM-5 weight and y = 4 wt.% Ba based on the strontium weight).

Manique *et al.* [63] synthesized sodalite zeolite as a catalyst for the transesterification of soybean oil. The optimum was obtained with a catalyst concentration of 4 wt.% and a molar ratio of 12:1 methanol-to-oil 95.5 wt.% of methyl ester was obtained within 2 h of reaction at 65 ºC. Al-Jammal *et al.* [64] prepared a serial-based catalyst from serial tufts by impregnation methods. The zeolite tufts were initially treated with HCl (16%) and then prepared by using several KOH/zeolite catalysts into KOH solutions. Different solutions of KOH with different molecules (1 × 10^{-6} M) were used. Further modification for the catalyst was carried out by heating the KOH/zeolite to 80 ºC for 4 h in a step 2 impregnation treatment. Catalysts were used to transesterification of the waste sunflower vegetable oil to produce biodiesel. Among the various catalysts prepared, the 1 × 10^{-4} M KOH/TZT catalyst gave a maximum biodiesel yield of 96.7% at 50ºC, a molar ratio of methanol-to-oil of 11.5:1, agitation speed of 800 rpm, catalyst weight 6.4 wt.%, 335 mm catalyst particle size and 2 h reaction time.

Du *et al.* [65] used NaY zeolite supported La_2O_3 as a heterogeneous catalyst for transesterification of castor oil to biodiesel. A granulating machine processed the La_2O_3/NaY spherical particle (3-5 mm) to produce castor oil biodiesel. The effect on the yield of the calcination temperature, catalyst concentration, ethanol-to-oil molar ratio, reaction temperature, and fatty acid ethyl ester (FAEE) was optimized by single-factor analysis. The addition of surfactant has a positive effect on the dispersion of La_2O_3 and the pore size of zeolite NaY. The synthesized catalyst showed remarkable reusability and crushing strength, which is essential for industrial use. Under optimized conditions of the catalyst concentration of 10wt.%, the molar ratio of ethanol-to-oil of 15:1, the reaction temperature of 70 ºC, and the FAEE yield was 84.6% for 50 min. Xie & Li [66] studied alumina support potassium iodide (KI/Al_2O_3) as a heterogeneous catalyst for biodiesel production from soybean oil. After loading 35 wt.% KI on alumina and calcinating at 773 K for 3 h, the catalyst gave the highest basicity and best catalytic activity for the reaction. Depending on the reaction variables such as soybean oil catalyst loading, the molecular ratio of methanol-to-oil and reaction time was studied. About 96% of conversions took place under optimal reaction conditions. The optimum reaction condition was per-formed at reflux methanol with a methanol-to-oil molar ratio of 15:1, a reaction temperature of 65 ºC, a reaction time of 8 h and a catalyst load of 2.5 wt.%.

Umdu *et al.* [67] performed experiments to study the activation of CaO and MgO catalysts that support Al_2O_3 in the transesterification of lipid of yellow, green microalgae, *Nannochloropsis oculata*. Biodiesel yields were higher when the catalyst supported with Al_2O_3 than pure CaO or MgO. Pure CaO and MgO catalysts were not active for microalgal lipid transesterification. However, catalysts with 80% load are the most active catalysts, which were 4-5 times more active than those with 50% load. At 80 wt.% load, the biodiesel yield was 23% for CaO/Al_2O_3 while 16% for MgO/Al_2O_3. The reaction temperature, catalytic load, and reaction time were maintained at 50 ºC, 2 wt.% and 4 h, respectively. When the methanol-to-lipid molar ratio was increased from 6:1 to 30:1, biodiesel yield was increased from 23% to 97.5%. Zabeti *et al.* [68] optimized the methyl ester yield produced by transistorizing the palm oil using a CaO/Al_2O_3 base catalyst. Response surface methodology (RSM) was used in combination with central composite design (CCD) to optimize the operating parameters. The molar ratio of alcohol-to-oil, the catalytic content of the reaction medium, and the reaction temperature were selected as variables and the selected response was methyl ester yield. The optimum values of the parameters were catalyzed 5.97 wt.%, alcohol-to-oil molar ratio 12.14:1 and reaction temperature of 64.29 ºC. Under these conditions, methyl ester yield was 98.64% within 5 h. The results of ICP-MS demonstrated, the leaching of the catalyst into the reaction was negligible and under certain reaction conditions and the reusability of the catalyst was successfully tested in two subsequent cycles.

Samart *et al.* [69] used CaO/mesoporous silica (CaO/SiO_2) catalyst as a heterogeneous catalyst to produce biodiesel by the methanolysis of soybean oil. The effect of CaO loading levels on the mesoporous silica catalyst, the catalyst amount to the substrate level and the reaction temperature and duration of soybean oil conversion were examined. Increased total conversion of soybean oil was obtained by increasing the temperature and reaction time. The optimum condition was found to be 15wt.% loadings of calcium on mesoporous silica catalyst, 5% (w/w) catalyst at 60 ºC reaction temperature for 8 h and the methanol-to-oil molar ratio of 16:1, which resulted in the highest yield of 95.2%. Witoon *et al.* [70] used bimodal meso-macroporous silica as a support to enhance the accessibility of CaO dispersed inside the pores. Unimodal porous silica with a similar mesopore diameter was used for comparison. The effect of CaO content and catalyst pellet size on the yield of fatty acids methyl esters (FAME) was investigated. It was found that the basic strength increases with increasing CaO content. About 30% of CaO in CaO/SiO_2 was highly dispersed in the mesopore of the catalyst, while 40% of CaO in CaO/SiO_2 was higher basicity as CaO highly concentrated on the mesoporous SiO_2 surface. Accordingly, 40 wt.% of CaO in CaO/SiO_2 shows a higher FAME yield than 30 wt.% of CaO in CaO/SiO_2. The CaO-loaded bimodal porous silica catalyst with a size of 325 μm achieved a high FAME of 94.15 in the first cycle. It retained an excellent FAME of 88.87% after five consecutive cycles under the reaction condition at 60 ºC, the methanol-to-oil molar ratio of 12:1 and catalyst amount of 5 wt.% for 4 h reaction time. Wu *et al.* [71] formulated a series of base catalysts based on potassium salts such as K_2CO_3, K_2SiO_3 and KOAc supporting mesoporous silica (SBA-15 and AlSBA-15) impregnation method and used to make as a catalyst for the transesterification of jatropha oil with methanol. The results showed that the Al element dopant in SBA-15 could protect the porous structure of the supported catalyst. The basicity and catalytic activity of AlSBA-15 silica were significantly improved after the loading of potassium compounds. The performance of K_2SiO_3 catalyst was superior to that of K_2CO_3 and KOAc catalysts. After calcinating at 600 ºC, K_2SiO_3/AlSBA-15 catalyst was found to be the optimal catalyst impregnated with 30 wt.% K_2SiO_3. The highest biodiesel 95.1 ± 1.4% yield was facilitated at 60 ºC, Catalyst loading ratio 3 wt.%, the methanol-to-oil molar ratio of 9:1 and the reaction time was 150 min. Reuse of the catalysts showed that K_2SiO_3/AlSBA-15 has a stable catalytic activity compared to conventional KOH and K_2CO_3 catalysts. After reusing for 5 cycles, the biodiesel yield was reduced by about 6% due to a slight decrease in its activity. The main reason for the decrease in the catalyst activity was leaching of potassium and the absorption of organic deposits on the surface of the catalyst.

Buasri *et al.* [72] developed a method to produce high-quality FAME from waste cooking palm oil. The continuous transesterification of FFA acidified with methanol was performed using calcium oxide, which supports activated carbon (CaO/AC) as a heterogeneous solid-base catalyst which was prepared according to the conventional incipient-wetness impregnation of aqueous solutions of $Ca(NO_3)_2{\cdot}4H_2O$ precursors on an activated carbon support. Results showed that the FFA conversion increased with increasing alcohol-to-oil molar ratio, catalyst bed height, and temperature. When the catalyst bed height was increased from 110 to 295 mm, the conversion increased rapidly from 55.1% to 85.0%. However, when it exceeded 295 mm, the reaction rate increased slightly. Therefore, in this study, the optimum catalyst bed height for biodiesel production was measured at 295 mm were found. The yield of FAME was 94% at a reaction temperature of 60 ºC, the molar ratio of methanol-to-oil of 25:1 and the residence time of 8 h. It was also reported that the catalytic activity of CaO/AC was 70.1% after the fourth reuse. Konwar *et al*. [73] studied that the waste shell of *T. striatula* used as raw to form both activated carbon (AC) and CaO. An activated carbon-supported CaO (CaO/AC) catalyst was used to transesterification the waste cooking oil. It was observed that 96% of methyl ester conversion could be obtained under optimum conditions such as 120 ºC, 40:1 methanol-to-oil ratio, 11 wt.% catalyst load and reaction time to 7 h. The catalyst was reusable and maintained its initial activity for approximately five cycles.

Hameed *et al*. [74] studied the transesterification of waste cooking palm oil using an activated carbon-supported potassium fluoride (KF/AC) as a catalyst. A central composite rotatable design was used to optimize the molar ratio of methanol-to-oil, the reaction time, the catalyst loading, and the reaction temperature during the reaction process. The reactor was pressurized to 10 bar using nitrogen gas. Response surface methodology (RSM) was used to find the optimum conditions for the transesterification of waste cooking palm oil to the methyl ester. The optimum conditions were 3 wt.% of catalyst loads, at 175 ºC of reaction temperature, a molar ratio methanol-to-oil of 8.85:1 and the reaction time of 1 h. Optimally, the predicted methyl ester yield was 83%. Baroutian *et al*. [75] used a KOH catalyst to support the palm shell activated carbon (KOH/AC) as a catalyst for the transesterification of palm oil. The central composite design (CCD) and the response surface methodology (RSM) were developed to investigate the effect of reaction temperature, catalyst loading and the ratio of methanol-to-oil molar ratio to produce biodiesel using a KOH/AC. The highest yield was obtained at a reaction temperature of 64.1 ºC, 30.3 wt.% catalyst loading, a molar ratio of methanol-to-oil of 24:1 and reaction time of 60 min. Under these optimal conditions, 98.03% product yield was obtained with catalyst leaching of 0.53 ppm.

Li *et al*. [76] used K_2CO_3 supported kraft lignin activated carbon (K_2CO_3/KLC) that was synthesized *in situ* by mixing with K_2CO_3 technical Kraft lignin (KL) and then calcinated at 800 ºC for 2 h under N_2 flow. The biodiesel yield of 99.6% was achieved by K_2CO_3/KLC at 0.6 wt.% at 65 ºC for 2 h, from methanol-to-rapeseed oil molar ratio of 15:1 and 3 wt.% catalyst. The catalyst can be reused 4 times and the biodiesel yields exceeded 82.1% for the fourth time. Navajas *et al*. [77] synthesized magnesium-aluminum hydrotalcite (Mg-Al HT) in the Mg-to-Al molar ratio of 1.5: 1-5: 1. After rehydration in boiling water, calcined oxides recovered the hydrotalcite structure in the form of meixnerite. The basicity of re-hydrated hydrotalcite was increased with the Mg-to-Al molar ratio. A general correlation was found between the basic properties of catalysts and their activation for sunflower oil methanolysis. Only re-hydrated hydrotalcite was significantly more active in this regard. Furthermore, activity increased with the Mg-to-Al ratio and degree of rehydrationrehydration. With more active samples, about 50% of oil can be converted after 8 h of reaction, with 60 ºC, 1 atm, the methanol-to-oil molar ratio of 12:1 and 2 wt.% under catalytic transesterification conditions. This conversion was increased up to 75% after 24 h when the catalyst uses 6 wt.% when the molar ratio of methanol-to-oil was increased to 48:1. Under these conditions, after 24 h, the biodiesel yield was 92%.

Zeng *et al*. [78] studied the activation of Mg-Al hydrotalcite (Mg-Al HT) catalyst for the transesterification of rapeseed oil. The Mg-Al hydrotalcite was prepared with different Mg-to-Al molar ratio. The hydrotalcite catalyst was calculated at 773K with an Mg-to-Al molar ratio of 3.0 was indicated the highest catalytic activity in transesterification. In addition, a study was performed to optimize the transesterification reaction conditions, and the optimized parameters were 6:1 methanol-to-oil molar ratio with a 1.5 wt.% catalyst at 65 ºC for 4 h under stirring speed of 300 rpm. The maximum ester conversion was 90.5%. Ma *et al*. [79] investigated the production of biodiesel from waste cooking oil by using calcined Mg-Al hydrotalcite as a heterogeneous catalyst. This study was formulated the calcined Mg-Al HT under optimal conditions to catalyze the waste cooking oil for biodiesel production. The Mg-Al HT with an Mg-to-Al ratio of 3: 1 showed a uniform mesoporous structure, excellent crystallinity, high surface area (270.5 m^2/g) and good catalytic activity at 500 ºC calcination. Under the optimum conditions, the methanol-to-oil molar ratio of 6:1, methanol-to-ethanol molar ratio of 4: 2, catalyst content 1.5%, reaction time 2.5hours, reaction temperature 80 ºC, where the highest biodiesel yield was 95.2%.

Trakarnpruk & Porntangjitlikit [80] prepared biodiesel from palm oil by transesterification with methanol in the presence of 1.5% K loaded-calcined Mg-Al hydrotalcite (K/Mg-Al HT). The fatty acid methyl ester content was 96.9% and the methyl ester yield was 86.6% for the oil molar ratio of 30:1 methanol at 100 ºC for 6 h and 7 wt.% of catalyst. Gao *et al*. [81] successfully used KF/Ca-Al hydrotalcite as a solid heterogeneous catalyst in the transesterification of methanol with palm oil to produce biodiesel. With the loading of the KF, the activity of Ca-Al mixture-oxide greatly increased. With the loading of KF, the activity of Ca-Al mixed-oxide greatly increased. A catalyst for the mass ratio of 80 wt.% (KF·6H_2O to Ca-Al mixed oxide), under optimum conditions of 338 K, catalyst load of 5 wt.% and methanol-to-oil molar ratio of 12:1, after 5 h of reaction, the yield of fatty acids methyl esters was reached 97.98%. For a mass ratio of 100 wt.% (KF·6H_2O to Ca-Al mixed-oxide), under the same reaction conditions, 99.74% of FAME yield was obtained just in 3 h, whereas biodiesel was yielded 97.14% under 1 h reaction time. Gao *et al*. [82] developed and studied KF/Ca-Mg-Al hydrotalcite (100% KF mass ratio), a series of base catalysts with different cation ratios. The effect of methanol-to-oil molar ratios on the cation ratio of Ca-Mg-Al hydrothorax and the yield of fatty acids methanol ester (FAME) from palm oil transesterification with methanol was investigated. The results of the transesterification reaction showed that all these types of catalysts had a very high efficiency for the yield of biodiesel, yielding 90% or more with a reaction time of 10 min at 338 K, a molar ratio of 12:1 methanol-to-oil and 5 wt.% catalyst content. Also, with an optimal ratio (2.2:0.8:1) of catalyst obtained by CCD method, in under the same reaction conditions, the FAME yield was obtained 99.6%.

Kawashima *et al.* [83] tested the heterogeneous base catalysts for developing an effective catalyst for biodiesel production. Thirteen metal oxides containing calcium, barium, magnesium, or lanthanum were prepared as catalysts, and catalytic activity was examined at 60 ºC with a 6:1 molar ratio of methanol-to-oil for 10 h for transesterification of rapeseed oil. Calcium containing catalysts $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and $CaO-CeO_2$ were found to be highly active and yield up to 90% of methyl esters achieved. Moreover, the catalyst durability tests were conducted by repeating the transesterification reaction several times with calcium-containing catalysts derived from the previous reaction mixture. The $CaZrO_3$ and $CaO-CeO_2$ showed high durability and yielded more than 80% due to the 5th and 7th time, respectively. There were found to have the potential to be used as heterogeneous base catalysts in biodiesel production processes. Sun *et al.* [84] prepared ZrO_2 supported La_2O_3 catalyst and utilized in the reactions with sunflower oil transesterification with methanol to produce biodiesel. It was found that at 600 ºC for 4 h, catalyst containing 21 wt.% La_2O_3 loaded on ZrO_2 was found with the highest basicity and catalytic activity for the transesterification reaction. Loading of La_2O_3 reduced the crystallite size of support ZrO_2 due to the formation of $La_2O_3-ZrO_2$ solid solution during calcination. When the La_2O_3 load increased from 7% to 21%, both sunflower oil conversion and FAME yields increased until a maximum of 96% was reached and 84.9%, respectively under the reaction condition of catalyst loaded of 5 wt.% with the methanol-to-oil molar ratio of 30:1 at a reaction temperature of 200 ºC for 5 h.

Wen *et al.* [85] obtained the mixed oxide of TiO_2-MgO by the sol-gel method to convert the waste cooking oil into biodiesel. Titanium ions were substituted for Mg ions due to the addition of Ti in the magnesia lattice, which causes defects on the catalyst surface there by, stability was improved. Based on the catalyst activity and stability, MT-1-923 was determined as the best catalyst, which has an Mg-to-Ti molar ratio of 1:1 and calcinated at 923 K. However, the catalyst activity of MT-1-923 slowly decreased during the reuse process. After regeneration, the activity of MT-1-923 was increased slightly compared to that of fresh catalyst due to the increase in the specific surface area and the average pore diameter. A biodiesel yield of 92.3% was observed using the MT-1-923 catalyst and optimal reaction conditions of the methanol-to-oil molar ratio of 50:1, 10 wt.% of TiO_2-MgO at 160 ºC for 6 h reaction time and stirring speed of 1500 rpm. Madhuvilakku & Piraman [86] synthesized TiO_2-ZnO mixed oxides nanocatalyst and ZnO nanocatalyst for biodiesel production palm oil. The reaction was carried out for 5 h at 60 ºC with a 6:1 methanol-to-oil molar ratio. When the catalyst loading was increased from 50 to 350 mg, the biodiesel conversion was gradually increased, yielding a maximum yield of 92.2% by TiO_2-ZnO mixed oxide nanocatalyst and 83.2% 250 mg of ZnO nanocatalyst, respectively. However, as the catalyst load was increased further, the conversion was decreased. TiO_2-ZnO mixed nanocatalyst 200 mg and ZnO nanocatalyst 250 mg were used to optimize the other reaction parameters. The TiO_2-ZnO catalyst exhibited good catalytic activities due to the substitution of Ti ions on the zinc lattice leads to creating a defect that is responsible for stable catalytic activity.

Su *et al.* [87] successfully formulated super microporous solid base $MgO-ZrO_2$ with pore size 1-2 nm by using a facile one-pot evaporation-induced self-assembly (EISA) method and applied to transesterification of soybean oil and methanol under the methanol-to-oil molar ratio of 20:1 and the catalyst 3 wt.% for 6 h reaction time. The surface area of super microporous microcrystalline $MgO-ZrO_2$ nanocatalyst was exceeded 200 m^2/g. Moreover, the sample, which calcinated at 400 ºC with the molar ratio of Mg-to-Zr at 0.5, showed a high biodiesel yield of about 99% at 150 ºC due to strong basicity and high surface area than the molar ratio at 1 and 1.5 of $MgO-ZrO_2$. Ren *et al.* [88] investigated continuous biodiesel production by transesterification soybean oil with methanol in a fixed bed reactor packed with D261 anion exchange resin as a heterogeneous catalyst. Conversion to biodiesel in 56 min under conditions was 95.2%. The biodiesel conversion was investigated under the conditions methanol-to-oil molar ratio of 9:1, co-solvent (*n*-hexane)-to-oil of 0.9 wt.%, reaction temperature of 323.15 K, resin loading of 80 g, feedstock flow rate of 1.2 mL/min. However, the activity of the resin was decreased quickly after 4 h without regeneration.

Jaya *et al.* [89] used Indion 810 as a catalyst which is a microporous, strongly basic anion exchange resin. The fatty acid methyl ester yield of pongamia oil was 85%, 2 wt.% of anion heterogeneous catalyst with 9:1 of ethanol-to-pongamia oil molar ratio stirring rate at 270 rpm resulted in a high yield at the optimum temperature of 75 ºC. Hartono *et al.* [90] investigated heterogeneous catalysts from various sources, such as Lewatit macroporous resin, Amberlite gel resin and natural zeolite bayah activity in the production of biodiesel from used cooking oils. The maximum biodiesel yield percentage of 85.94% was achieved by Lewatit macroporous anion exchanger with 6 M of NaOH under reaction conditions at 60 ºC for 2 h at 700 rpm oil-to-methanol ratio of 1:7 and 3 wt.% of catalyst load. The maximum yield of biodiesel from natural zeolite bayah with 6M of NaOH solution and Amberlite gel with 6M HCl was 6.19% and 65.22%, respectively.

Chin *et al.* [91] used a central composite rotatable to study the effect of the ratio of methanol to oil, reaction time, catalyst magnitude and temperature for the transesterification of waste cooking palm oil using oil palm ash as a catalyst. The reaction was performed at 10 bar. The study was revealed that oil palm ash has a high percentage of potassium and a relatively low percentage of aluminum, zinc and magnesium. Besides, due to the high rate of oxygen, it was assumed that potassium, zinc, magnesium, silicon and aluminum were primarily oxidized. It was found that K_2O is responsible for the catalyst's high catalytic activity and initiation. The optimum conditions for the transesterification of palm oil to biodiesel were achieved under 5.35 wt.% of catalyst, 60 ºC, the molar ratio of methanol-to-oil 18:1 and reaction time 0.5 h. Predicted and experimental biodiesel yields were found to be 60.07 wt.% and 71.74 wt.%, respectively. Boey *et al.* [92] used boiler ash (BA) as a pseudo-homogeneous base catalyst for the transesterification of palm oil. As shown in this study, the calcination of BA was not given a significant increase in methyl ester conversion but was increased to increase the reusability of the catalyst. Furthermore, it was found to be intolerant to water and free fatty acids. Boiler ash was successfully transesterified under mild reaction conditions to produce 90% methyl esters such as 3 wt.% dry BA, 15:1 methanol-to-oil molar ratio, 60 ºC reaction temperature, and 30 min reaction time. As a result, presence of K_2O and other basic metal oxides (SiO_2, MgO, CaO and P_2O_5) during BA drying significantly increased the catalytic activity as higher basicity and basic strength. However, BA was acted favourably as a catalyst for transesterification, it cannot be reused as the catalyst leaching out of the system during reactions.

Vadery *et al.* [93] prepared fuel-grade biodiesel as a cost-effective and efficient method by transesterification jatropha oil at room temperature in the presence of a coconut husk ash as a heterogeneous catalyst under mild reaction conditions without the use of any co-solvent. Coconut husks were subjected to calcination at 350 ºC resulted in ash contained various compounds KCl, K_2SO_4, K_2S_3, $KAlO_2$, $FeCa_2Al_2BSi_4O_{15}OH$, $K_2Si_2O_5$, $K_4CaSi_3O_9$ *etc*. It was found that biodiesel content was more than 97% within 30 min of reaction time at 45 ºC with a 12:1 methanol-to-oil molar ratio and 7 wt.% of coconut husk ash. Changmai *et al.* [94] investigated the catalytic activity of orange peel ash (OPA) derived from biomass containing a porous structure as a heterogeneous catalyst for transesterification of soybean oil to biodiesel. The OPA contained K_2O and CaO as the major components which play a major catalytic role inthe production of biodiesel from soybean oil. About 98% of the conversion of soybean oil into biodiesel was obtained under optimal reaction conditions of 6:1 methanol-to-oil molar ratio, 7 wt.% catalyst loading, 7 h reaction time at room temperature. The catalyst was reused for five consecutive cycles and showed good stability in biodiesel production.

Miladinovi *et al.* [95] investigated the catalytic activity of walnut shell ash by sunflower oil methanolysis in biodiesel production. Walnut shell ash provides a very fast reaction and a high FAME content of over 98% under the 12:1 of methanol-to-oil molar ratio in the presence of 5wt.% walnut ash at 60 ºC of reaction temperature for 10 min. The catalyst consisted of metal oxides (mainly CaO and K_2O). Since the reaction occurred when the triacylglycerol mass exchange limit was not reached, a pseudo-first model was used to describe the kinetics of the reaction. The catalyst was successfully reused four times after regenerating the catalyst at 800 ºC. Etim *et al.* [96] determined that ripe banana peels could be used as a green-based catalyst in *Azadirachta indica* oil methyl ester (AIOME). Biodiesel synthesis was carried out using neem oil, methanol and calcined ripe plantain peel ash (CRPPA) at 700 ºC in a two-step transesterification process. Neem oil having high free fatty acid content was initially reduced to 0.90 wt.% in an esterification reaction *via* methanol-to-oil 2.19 v/v, $Fe_2(SO_4)_3$ 6 wt.%, 15 min reaction time and temperature 65 ºC. In the second step, an AIOME yield of 99.2 wt.% was obtained from combining the operating variants of the transesterification process, methanol: oil 0.73 v/v, CRPPA 0.65 wt.% and the reaction time were 57 min, while the reaction temperature was maintained at 65 ºC. The calcinated temperature was significantly affected by the elemental composition of CRPPA, where the main components of CRPPA samples are O, Mg, P, S, K, Si, and Cl. Except for 900 ºC, potassium has the highest mass fraction regardless of the calcinated temperature, but the highest mass fraction was observed at 700 ºC. The calcination resulted in a microscopic structure of the catalyst increased the surface area of the catalyst, thereby increasing the catalyst activity.

Deka & Basumatary [97] used a heterogeneous catalyst derived from the trunk of *Musa balbisiana* Colla (a variety of banana plant) for biodiesel production from yellow oleander (*Thevetia peruviana* Schum.) seed oil. The catalyst contained K^+, Na^+, CO_3^{2-} and Cl^- as the main compound, and eleven other metals such as Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb present only in a small amount. Metals exist as carbonates, chlorides or oxides, or finely divided carbon particles 96 wt.% of oil was converted to biodiesel at 32 ºC in 3 h with 20 wt.% of catalyst in the presence of 20 mL/g of oil in methanol. Abdelhady *et al.* [98] used the agricultural waste CaO rich sugar beet as a promising heterogeneous catalyst for the efficient production of biodiesel. The CaO rich sugar beet showed excellent catalytic activity for biodiesel production through the process of transesterification of agricultural waste using sunflower oil and methanol. Biodiesel conversion of 93% was achieved under optimal conditions (catalyst loading 1 wt.%, methanol-to-oil molar ratio 4.5: 1, at 75 ºC for 1 h. The high catalytic activity of the prepared catalyst was obtained by calcination at 800 ºC due to its large surface area (27.9 m^2 g^{-1}) and small average particle size (33 nm) as well as its high basicity. The relatively short reaction time demonstrated the improved kinetics of the process using the proposed agricultural waste gave its economical viability. Also, the proposed CaO rich sugar beet agro-industrial residue can be reused twice while retaining its catalytic activity.

Jayaraman *et al.* [99] studied lipase enzyme for biodiesel production. Waste cooking oil was reacted with methanol in lipase enzymes as a catalyst to produce waste cooking oil methyl ester through enzymatic transesterification. After several trials, methanol as alcohol, 1.5 wt.% enzyme concentration at 65 ºC of reaction time, 3:1 molar ratio of alcohol-to-oil stirrered at 1000 rpm and 4 h reaction time were used as the perfect reaction conditions to facilitate 88% of the methyl ester. Sebastian *et al.* [100] conducted a study to determine a suitable lipase from *Thermomysis lanugonosus* lipase, *Candida antarctica* lipase, pancreatic lipase and *Rhizopus oryzae* lipase for biodiesel production from rubber seed oil obtained mechanically from preserved rubber seed cakes. The extracted oil was subjected to enzyme transesterification using four different lipases. The transesterification process was optimized by considering three variables that affect biodiesel production, such as methanol-to-oil molar ratio, catalyst concentration (%w/v), and solvent content (%v/v). *Thermomysis lanugonosus* lipase was the most suitable for the transesterification of rubber seed oil with a biodiesel conversion of 92.83% at enzyme concentrations of 5% (w/v) a molar ratio of 4 in a thermally stable reaction medium. The FAME conversion for *Candida antarctica* lipase, pancreatic lipase and *Rhizopus oryzae* lipase was 79.69%, 48.9% and 23.22%, respectively.

Wancura *et al*. [101] focused on the evaluating parameters of enzymatic biodiesel production from soybean oil using the lipase extracted from *Thermomyces lanuginosus* in its soluble form as a catalyst. The commercial CalleraTM Trans L (CalT) lipase emerges as an interesting alternative catalyst for the hydrolysis-esterification reaction. Central composite statistical design (CCSD) was evaluated for the use of CalleraTM Trans L lipase for biodiesel synthesis and optimize the key variables such as temperature, methanol-to-oil molar ratio, and catalyst concentration. In the hydrolysis-esterification process, a combination of factors contributing to the maximum biodiesel yield. CalleraTM Trans L lipase was observed to exhibit high catalytic activity. The optimum variables for biodiesel synthesis were 35 ºC temperature, methanol-to-oil molar ratio 4.5:1 and the catalyst load was 1.45 wt.%, resulting in the reaction yield of 96.9% biodiesel in 24 h. Arumugam & Ponnusami [102] studied waste sardine oil for biodiesel production and evaluation of its engine performance. Waste sardine oil, a byproduct of fish industry, was used as a low-cost feed for biodiesel production. It has a relatively high free fatty acid content (32 mg KOH/g). The lipase enzyme immobilized on activated carbon was used as a catalyst for the transesterification reaction. The optimum molar ratio, water content, and temperature of the reaction were found to be 9: 1, 10(v/v%) and 30 ºC, respectively. The reusability of immobilized lipase was studied and found that the FAME yield was decreased by about 13% after 5 cycles of reuse. A variable compression engine studied the engine performance of the manufactured biodiesel and the results confirmed that waste sardine oil is a potential alternative and low-cost feeder for biodiesel production.

Devi *et al*. [103] synthesized a glycerol-based heterogeneous "green" catalyst for the preparation of biodiesel from fatty acids. The glycerol-based sulfonic acid groups (-SO_3H) were synthesized in a high carbon catalyst, obtained as a byproduct of biodiesel processing and their utility was projected as an efficient solid acid catalyst. The glycerol based carbon catalyst was obtained by *in situ* partial carbonization and sulfonation with sulfuric acid in a ratio of 1:4 (w/w) for 40 min. The yield of the catalyst was about 50% by the weight of glycerol used for the reaction. The catalyst was evaluated at 10 wt.% (99% conversion in 4 h) when esterifying the palmitic acid with methanol for biodiesel production at 65 ºC. The efficacy of a glycerol based carbon catalyst for the production of biodiesel from palmitic acid and methanol was studied with two typical solid acid catalysts *viz*. Amberlist-15 and ZSM-5 zeolite. The carbon catalyst exhibited higher esterification activity and did not lose its activation even after 8 times of recycling. Mardhiah *et al*. [104] prepared a carbon-based acid catalyst using oil-free *Jatropha curcas* (JC) seed cake waste. The catalyst was used to esterify JC oil to reduce the high free fatty acid content to an acceptable level for biodiesel production. The FFA conversion was reached 99.13% under optimal 12:1 methanol-to-oil molar ratio, 7.5wt.% catalyst loading, and stirring speed of 350rpm. The catalyst was determined to surpass conventionally used sulfuric acid catalyst in terms of the reaction time required to obtain the highest conversion yield. The hydrophilic nature of the catalyst also contributed the stability of the reusable catalyst until the 4th cycle. The recycling of the catalyst and its cheap nutrients make the whole process simpler, cost-effective, and environmentally friendly.

Devi *et al*. [105] synthesized a green recyclable SO_3H-carbon catalyst obtained in one step from glycerol to produce biodiesel from high FFA-containing karanja (*Pongamia glabra*) oil. Simultaneous esterification and transesterification were applied to synthesize biodiesel from 7.5% free fatty acid (FFA) containing karanja oil using a water-resistant and reusable carbon-based solid acid catalyst derived from glycerol in a single step. The optimum reaction parameters for obtaining biodiesel in >99% was yield by simultaneous esterification and transesterification were methanol-to-oil 1:45 mole ratio, catalyst loading of 20 wt.%, temperature 160 ºC and the reaction time of 4 h. After the reaction, the catalyst can be easily recovered by filtration and reused five times outwardly any deactivation under optimal conditions. Dehkhoda *et al*. [106] tested a promising catalyst based on a biomass pyrolysis byproduct, biochar for biodiesel production. Two carbon-based acid catalysts were prepared by sulfonating pyrolysis char with concentrated or fuming sulfuric acid. The catalyst sulfonated with concentrated sulfuric acid showed a significant conversion in FFA esterification and showed limited transesterification activity. Using a stronger sulfonating reagent such as fuming sulfuric acid resulted in greater transesterification activity. Subsequent catalytic tests were performed to determine the sulfonation time (5 and 15 h) and the surface area for the transesterification reaction. The surface area of biochar was expanded by pore development using 10 M KOH by chemical treatment. As a result, the catalyst with the highest surface area and acidity had the highest catalytic activity to produce biodiesel from canola oil. Furthermore, a higher surface area catalyst was shown a higher transesterification activity than a catalyst with similar acidity. The alcohol ratio, reaction time and catalyst loading on the esterification reaction catalyzed by the sulfonated biochar were also investigated. Catalyst loading of 5wt.%, a reaction time of 3 h and an alcohol-to-oil ratio of 18: 1 was the optimum reaction condition for giving the best results. A slight increase in FFA conversion was observed at molar ratio beyond 18:1 and at reaction times between 9 and 15h, but the changes were not significant due to measurement-related variability. The catalyst was found to be able to reduce the FFA level from approximately 12.2 wt.% to approximately 1.04 wt.% (which corresponds to a reduction in acid value from 24.5 to 2.04mg KOH/g and conversion of 92%).

Conclusion

Because fossil fuels are a limited energy source, many researchers have focused on sustainable renewable energy for decades. Biodiesel is one of the promised energy sources that can be used as a substitute for conventional diesel. However, biodiesel can be produced with a variety of technologies, and transesterification is a popular one. The yield of biodiesel produced depends on many factors, including feedstock type, alcohol type, alcohol-to-oil molar ratio, catalyst type, catalyst content, reaction time, reaction rate, *etc*. The purpose of adding the catalyst to the reaction is to minimize the activation energy required to complete the reaction in a short period. Therefore, the catalyst plays a significant role in the transesterification reaction. Several studies have examined and revealed that different types of catalysts can be used for the transesterification reaction. Depending on the type of catalyst, there are advantages and disadvantages to transesterification. A homogeneous catalyst is preferable, as it can operate under mild reaction conditions however, a downstream purification process is required to remove the catalyst from the product. The heterogeneous catalyst can be easily removed and reused, but heterogeneous catalysts have a disadvantage because of the mass transfer resistance due to the presence of three layers. As a catalyst, the enzyme facilitates high yields at low reactive temperatures and does not affect the FFA content as well as the water content. Moreover, the enzyme is found not suitable for large-scale production as it constitute a high cost.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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