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Review Article

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Transesterification with heterogeneous catalyst in production of biodiesel: A Review

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ABSTRACT

Biodiesel, an alternative and renewable fuel for diesel engines, has become more attractive in recent times because of its renewability, biodegradability, nontoxicity and carbon neutrality. Biodiesel consists of mono alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from biological resources such as plant seed oils, animal fats or even waste cooking oils by transesterification with methanol. Transesterification reactions are catalyzed by acids, bases and enzymes. Heterogeneous catalysts are promising and receiving attention for the production of biodiesel. In the present paper, an attempt is being made to review on heterogeneous catalyst used in the production of biodiesel.

Keywords: Biodiesel; FAME; Transesterification; Heterogeneous catalyst.

INTRODUCTION

Biodiesel, mixture of fatty acid methyl esters (FAME), is an alternative and renewable fuel for diesel engines and has been attracted in recent times due to diminishing petroleum reserves and detrimental environmental impacts of petro-diesel. Biodiesel is environmental friendly, free of sulfur and aromatics, and hence ideal for heavily polluted cities. It is biodegradable and non-toxic [1-3]. Biodiesel is produced from any fat or oil through a process called transesterification. Transesterification is a process in chemistry for direct conversion of one ester to another. Such a process makes a synthetic methodology shorter by at least one step. Transesterification process is a must in the production of biodiesel. In the production of biodiesel, oils and fats are transesterified with methanol in the presence of an acid, base, or enzyme (lipase) catalyst to afford fatty acid methyl esters (FAME) and glycerol as a byproduct [4, 5]. Alcohols utilized for transesterification process are generally methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages. This process has been widely used to reduce the high viscosity of oils and fats, thereby enhancing the physical properties of renewable fuels to improve engine performance [6-8].

The conventional catalysts for transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H_2SO_4) [8, 9-12]. However, basic catalysts are generally corrosive to equipment and also react with free fatty acid to form unwanted soap as by-products that require expensive separation [13, 14]. Homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems [15, 16]. Enzymes or lipases are naturally occurring substances. They have excellent catalytic activity and stability in non-aqueous media, which facilitate the esterification and transesterification process during biodiesel production. Enzyme-based transesterification is carried out at moderate temperatures with high yields, but this method cannot be used in industry today due to high enzyme costs, and the problems related to its deactivation caused by feed impurities [17, 18]. Therefore, to overcome all these problems including cost, people are working on the development of economically viable as well as ecofriendly solid catalysts for biodiesel industries.

Heterogeneously catalyzed transesterification

Heterogeneous catalysts are promising and advantageous for biodiesel production because they could be operated in continuous processes, could give high quality of products; they are reusable, environmentally benign and are more effective than acid catalysts and enzymes. Besides, the use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization or triglyceride saponification. They can be designed to give higher activity, selectivity, and longer catalyst lifetimes [17, 19, 20-24]. A large number of acid and base heterogeneous catalysts for the production of biodiesel have been reported in the literature.

Karmee *et al.* [25] studied transesterification of *Pongamia* oil at 120 ^{o}C with 1:10 molar ratio of oil to methanol using ZnO, Hβ-Zeolite, and Montmorillonite K-10 as catalyst (11.5 wt.% of oil) to form biodiesel. The reaction time taken was 24 h and the conversion was 83% for ZnO, while Hβ-Zeolite and Montmorillonite K-10 catalyzed transesterifications gave low conversions of 59% and 47% respectively. Zeolite beta modified with La (La/zeolite beta) was investigated by Shu *et al.* [26] as a solid acid catalyst for methanolysis of soybean oil and only 48.9 wt.% of biodiesel was obtained.

Jitputti *et al.* [27] compared the catalytic activities of several acidic and basic solids catalysts such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2 for transesterification of crude palm kernel oil and crude coconut oil with methanol. Among the catalysts, sulfated zirconia (ZrO_2/SO_4^{2-}), a super acid gave the highest yield of methyl ester due to its high acid strength. The reaction was carried out at 200 ^{o}C with 1 wt.% catalyst content, and 6:1 of methanol/oil ratio in a high pressure reactor. After 1 h reaction time, 90.3 and 86.3 wt.% of methyl ester was obtained from crude palm kernel oil and crude coconut oil respectively. Zirconia alone gave lower yield. Crude palm kernel oil yielded higher methyl ester than crude coconut oil due to the higher free fatty acid and water content of crude coconut oil which reduced the methyl ester yield.

Peng *et al.* [28] prepared and studied SO_4^{2-}/TiO_2-SiO_2 as a solid acid catalyst for the production of biodiesel from low cost feedstocks (50% oleic acid + 50% refined cotton seed oil) with high free fatty acids (FFAs) in autoclave reactor at 200 ^{o}C with 9:1 molar ratio of methanol to oil and 3 wt.% catalyst concentration. 92% FAME was obtained within 70 min. The effect of FFA amount on the yield of esters was studied by adding 10, 30, 50 and 80 wt.% oleic acid to refined cottonseed oil under similar reaction conditions and it was observed that the FFA content increased the yield of methyl ester and the rate of esterification of oleic acid was higher than the rate of transesterification of cottonseed oil due to the better solubility of FFAs of cottonseed oil in methanol.

Kafuku *et al.* [29] studied production of biodiesel from *Moringa oleifera* oil using sulfated tin oxide enhanced with SiO_2 (SO_4^{2-}/SnO_2-SiO_2) as super acid solid catalyst. The reaction parameters studied were reaction temperature (60 to 180 ^{o}C), reaction period (1 to 3 h) and methanol to oil ratio (6:1 to 24:1). With reaction conditions of 150 ^{o}C temperature, 150 min reaction time and 19.5:1 methanol to oil ratio, the yield up to 84 wt.% of *Moringa oleifera* methyl esters was obtained, while catalyst concentration and agitation speed are kept at 3 wt.% and 350-360 rpm respectively. This study presents the possibility of converting a relatively new oil feedstock, *Moringa oleifera* oil to biodiesel and thus reducing the world's dependency on existing edible oil as biodiesel feedstock.

Lam *et al.* [30] demonstrated SO_4^{2-}/SnO_2-SiO_2 as a potential catalyst using mixed methanol-ethanol as an alternative way to produce greener biodiesel from waste cooking oil. The transesterification reaction was carried at 150 °C using 6 wt.% of catalyst. Optimum yield of 81.4% biodiesel was produced with methanol to ethanol to oil molar ratio of 9:6:1 in a relatively short reaction time of 1 h. This simple approach not only minimizes the limitation of using ethanol in transesterification catalyzed by solid acid catalyst, but also produces biodiesel in a more sustainable and greener way.

Nakagaki *et al.* [31] synthesized and investigated sodium molybdate (Na_2MoO_4) as a heterogeneous catalyst for the methanolysis of different types of lipids derived from soybean oil such as refined soybean oil (0.7 mg KOH/g acid value), degummed soybean oil (1.0 mg KOH/g acid value) and used frying oil (1.5 mg KOH/g acid value). The reaction was carried out at 65 ^{o}C with 54:1 of methanol/oil ratio, 5 wt.% catalyst contents in 3 h. The conversion achieved for refined soybean oil, degummed soybean oil and used frying oil were 95.6, 92.6, and 94.6 wt.% respectively.

Serio *et al.* [32] examined application of vanadyl phosphate (VOP) as catalyst in the transesterification of soybean oil and yielded 80% methyl ester only after 1 h reaction time even though the specific surface area of catalyst was low (2-4 m^2/g).

Ramu *et al.* [33] studied zirconia supported tungsten oxide (WO_3/ZrO_2) as a solid acid catalyst for esterification of palmitic acid with methanol and using 5 wt.% catalyst in 6 h, a conversion upto 98% was obtained.

Melero *et al.* [34] investigated transesterification of refined and crude vegetable oils with a sulfonic acid-modified mesostructured catalyst. This catalyst yielded fatty acid methyl esters over 95 wt.% for oil conversion close to 100% under the best reaction conditions (temperature 180 ^{o}C, methanol/oil molar ratio 10, and catalyst loading 6 wt.% with regard to the amount of oil). In presence of free fatty acids in the oils, the sulfonic acid-modified mesostructured catalyst showed high activity toward simultaneous esterification and transesterification. These sulfonated mesostructured materials are promising catalysts for preparation of biodiesel.

Garcia *et al.* [35] reported that sulfated zirconia, synthesized by a solvent-free method (S-ZrO_2), is very active in the transesterification of soybean oil and the esterification of fatty acids. The conversions obtained in the alcoholysis catalyzed by S-ZrO_2 under optimized conditions (120 ^{o}C, 1 h, 5 wt.% of catalyst) were 98.6% (methanolysis) and 92% (ethanolysis) with an immediate separation of the glycerin. The performance of ethanolysis was not as good as in methanolysis due to the higher water content of ethanol compared to methanol.

Chen *et al.* [36] synthesized a solid catalyst copper vanadium phosphate (CuVOP) and investigation showed that the catalyst is very active in the transesterification reaction for biodiesel production from soybean oil. The maximum conversion of 65.5% is obtained at loading of 1.5 wt.%, methanol/oil molar ratio of 6.75 at 65 ^{o}C and reaction time of 5 h.

Zhang *et al.* [37] studied *Zanthoxylum bungeanum* seed oil (ZSO) with high free fatty acids (FFA) for biodiesel production by ferric sulfate-catalyzed esterification followed by transesterification using calcium oxide (CaO) as a basic catalyst. The acid value of ZSO with high FFA (41.02 mg KOH/g) can be reduced to less than 2 mg KOH/g by one-step esterification at 95 ^{o}C in 2 h using methanol to ZSO molar ratio of 40.91:1 with ferric sulfate 9.75 wt.% of ZSO. Transesterification of pretreated ZSO using CaO as a catalyst was optimized by Response surface methodology, and the optimal conditions of the variables were as follows: methanol to oil molar ratio 11.69:1, catalyst amount 2.52%, and reaction time 2.45 h. Under optimal conditions, the conversion to biodiesel reached above 96%. The results supported that vegetable oil with high FFA can be used for biodiesel production by solid acid-catalyzed esterification followed by solid alkali-catalyzed transesterification. This study provided a friendly method to biodiesel production from raw feedstocks with high FFA.

Brahmkhatri *et al.* [38] synthesized 12-tungstophosphoric acid anchored to MCM-41 as a heterogeneous acid catalyst which exhibits significant activity for biodiesel production by esterification of free fatty acid, palmitic acid with methanol. The esterification of palmitic acid (0.01 mol, 2.5 g) with methanol (0.4 mol, 16.2 mL) was carried out at 60 ^{o}C for 4 h. The catalyst shows high activity in terms of 100% conversion toward palmitic acid. Studies also reveal that the catalyst could be used for biodiesel production from waste cooking oil without any pretreatment. The catalyst can be employed for the feedstocks that are rich in free fatty acids where simultaneous FFA esterification and triglycerides transesterification using a heterogeneous acid catalyst provides an alternative single step process for biodiesel production.

Various basic heterogeneous catalysts have been reported in literature for biodiesel synthesis. Kouzu *et al.* [39] examined transesterification of edible soybean oil with refluxing methanol in the presence of calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$). The yield of FAME was 93% for CaO, 12% for $Ca(OH)_2$, and 0% for $CaCO_3$ at 1 h of reaction time. CaO was used for further tests in transesterification of waste cooking oil with acid value of 5.1 mg KOH/g. The yield of FAME was above 99% at 2 h of reaction time, but a portion of catalyst changed into calcium soap by reacting with free fatty acids present in waste cooking oil at initial stage of transesterification. Owing to the neutralizing reaction of the catalyst, concentration of calcium in FAME increased from 187 ppm to 3065 ppm. As quality of biodiesel and lifetime of the catalyst are important considerations, the catalyst should be guarded from the neutralizing reaction with free fatty acids.

Liu *et al.* [40] investigated SrO as a solid catalyst for transesterification of soybean oil to biodiesel. BET surface area of the catalyst was 1.05 m^2/g. A conversion of 95% was obtained at 65 ^{o}C with catalyst content of 3 wt.% and molar ratio of methanol to oil of 12:1 within reaction time of 30 min. Slightly reduced yield of biodiesel was observed when the SrO catalyst is subsequently reused for 10 cycles.

The TiO_2-MgO mixed oxide catalysts [41] prepared by the sol-gel method were successfully used for biodiesel production. The addition of Ti resulted in the substitution of Ti ions for Mg ions in the magnesia lattice, thus leading to defects on the catalyst surface. These defects can improve the stability while maintaining an acceptable catalytic activity. The best catalyst was determined to be MT-1-923, which comprised of Mg/Ti molar ratio of 1 and calcined at 923 K, based on an assessment of the activity and stability of the catalyst. For the MT-1-923, the catalytic activity decreased slowly within the reuse processes. After regeneration, the activity of MT-1-923 slightly increased compared with that of the fresh catalyst due to an increase in the specific surface area and average pore diameter.

The mixed oxides catalyst, TiO_2-MgO, showed tremendous potential in large-scale biodiesel production from waste cooking oil.

Lingfeng *et al*. [42] investigated the possibility of using KF/γ-Al_2O_3 as heterogeneous catalysts for the transesterification of cottonseed oil with methanol. The operation variables used were methanol/oil molar ratio (6:1-18:1), catalyst concentration (1-5 wt.%), temperature (50-68 ^oC). The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 12:1, catalyst (4 wt.%), 65 ^oC temperature and reaction time (3 h), with the catalyst KF/γ-Al_2O_3 (mass ratio 50.36%).

Liu *et al*. [43] studied transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Biodiesel yield exceeded 95% in 3 h using 12:1 molar ratio of methanol to oil and 8 wt.% of catalyst at 65 ^oC. It is reported that the catalyst lifetime was longer than that of calcined K_2CO_3/γ-Al_2O_3, KF/γ-Al_2O_3 catalysts. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h was not affected much in the repeated experiments.

KF/ZnO catalyst [44] has been reported as solid base catalyst for the transesterification of palm oil with methanol to produce biodiesel. 35 wt.% of KF was loaded on ZnO and good conversions were achieved. The experimental study revealed that the optimum reaction conditions for transesterification of palm oil to biodiesel were methanol/oil ratio of 11.43, reaction time of 9.72 h, catalyst amount of 5.52 wt.% and reaction temperature was fixed at 65 ^oC. The optimum biodiesel yield was found to be 89.23%.

Guomin *et al*. [45] studied transesterification of palm oil with methanol to biodiesel over a KF/Al_2O_3 heterogeneous base catalyst. The biodiesel yield reached its maximum value of over 90% at the optimal condition, when the load ratio of KF/Al_2O_3 was 0.331 (wt./wt.), the molar ratio of methanol/oil was 12:1, the amount of KF/Al_2O_3 catalyst was 4 wt.% of oil, the reacted temperature was 65 ^oC, and the reaction time was 3 h.

Teng *et al*. [46] investigated KF/γ-Al_2O_3 as an active catalyst to prepare biodiesel from soybean oil. The optimal conditions of transesterification reaction were as followed: the load ratio was 72.68% (KF to γ-Al_2O_3, wt/wt), molar ratio was 12:1 (methanol/oil), reaction temperature was 65 ^oC, catalyst concentration was 2 wt.% of oil, and reaction time was 3 h. Under these conditions, the yield of biodiesel could reach over 99%.

Sun *et al*. [47] studied and reported that the KF loaded on Eu_2O_3 was an active catalyst for the production of biodiesel from rapeseed oil. After calcination at 600 ^oC for 4 h, the catalyst with 15 wt.% KF loaded on Eu_2O_3 was found to be the one with highest basicity and catalytic activity for the transesterification reaction. When the reaction was carried out in the reflux of methanol, with a molar ratio of methanol/oil of 12:1, a catalyst amount of 3 wt.% (of oil), and a reaction time of 1 h, the conversion of rapeseed oil to biodiesel was 92.5%.

Gao *et al*. [48] investigated that biodiesel can be produced from trans- esterification of palm oil with methanol over KF/hydrotalcite catalyst. The effective factors, such as KF/hydrotalcite load ratio, methanol/oil molar ratio, catalyst amount, reaction time, and reaction temperature, were investigated. When the reaction was carried out at 65 ^oC, with 12:1 molar ratio of methanol to oil, reaction time of 3 h, and catalyst amount of 3 wt.% of oil, the yield of fatty acid methyl esters could reach 85%, and when the reaction was kept for 5 h, 92% yield was obtained.

Gao *et al*. [49] also studied a series of solid base catalysts, KF/Ca-Mg-Al hydrotalcite (KF mass ratio of 100%) with different cation ratios for the transesterification reaction of palm oil with methanol. The catalyst could yield over 90% of biodiesel in 10 min under the following reaction conditions: reaction temperature, 65 ^oC; methanol/oil molar ratio, 12:1; and catalyst amount, 5% (wt.% of oil). The catalyst with an optimal cation ratio (2.2:0.8:1) was obtained by the central composite design method, and at the same reaction conditions, the FAME yield could reach 99.6%. This catalyst largely shortened the reaction time of the biodiesel production and showed a hopeful future of the new producing method of biodiesel.

Wan *et al*. [50] examined production of biodiesel from soybean oil by transesterification over sodium aluminate as a heterogeneous catalyst. The solid base showed high activity for the alcoholysis of soybean oil. The reaction was carried out at a reflux temperature with a 12:1 molar ratio of methanol/oil and 1.5 wt.% of catalyst for a reaction time varying from 10 to 60 min, in which the methyl ester yield reached 82.9-93.9%. The catalytic durability tests showed slight decrease in activity by repeating the transesterification reaction for three times.

Reddy *et al*. [20] studied transesterification of soybean oil with methanol to biodiesel at room temperature (23-25 ^oC) using polymer-supported azidoproaza- phosphatrane as a catalyst. This catalyst was recycled 11 times, although its activity decreased with time.

Kawashima *et al.* [51] studied the catalytic activity of calcium based metal oxides such as $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and $CaO-CeO_2$ in the methanolysis of rapeseed oil. The authors also studied the change of activity on replacement of Ca with barium, magnesium, or lanthanum. The reaction was carried out in a batch reactor at 60 ^oC with 6:1 molar ratio of methanol to oil for 10 h, in which the methyl esters yield reached 79-92%. It was found that $CaZrO_3$ and $CaO-CeO_2$ show high durability, ester yields greater than 80% and have the potential to be used in biodiesel production processes as heterogeneous base catalysts. $CaTiO_3$ had a base strength in the range of 6.8-7.2. $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaCeO_3$ had the highest base strengths, in the range from 7.2 to 9.3. However, the Ba, Mg, and La series catalysts showed the weakest base strengths, which were less than 6.8. These results suggest that the Ca series catalysts have high catalytic activity for the transesterification reaction, but the other catalysts have low activity.

Dossin *et al.* [52] investigated and reported MgO-catalyzed transesterification reaction, at industrially relevant conditions, in batch and continuous stirred tank reactors. A kinetic model based on the three steps 'Eley-Rideal' type mechanism assuming methanol adsorption as rate-determining step was proposed. Two processes were simulated, first for transesterification of ethyl acetate with methanol in a batch slurry reactor and second, transesterification of triolein with methanol to form methyl oleate in a continuous slurry reactor and results were used to simulate biodiesel production from rapeseed oil. The simulations indicate that a production of 500 tonnes methyl acetate per year can be reached at ambient temperature in a batch reactor of 10 m^3 containing 5 kg of MgO catalyst, and that a continuous production of 100,000 tonnes of biodiesel per year can be achieved at 50 ^oC in a continuous stirred reactor of 25 m^3 containing 5700 kg of MgO catalyst. The results indicate that for both processes, a heterogeneous magnesium oxide catalyst shows promising potential for industrial scale.

K_2CO_3 supported on MgO has been developed as the most efficient catalyst by Liang *et al.* [53] for synthesis of biodiesel from soybean oil and reported 99.5% yield of biodiesel. The catalytic activity of the K_2CO_3/MgO was higher than that of K_2CO_3 due to the interaction between K_2CO_3 and MgO and because of the high degree of dispersion of the active sites on the surface of MgO. Maximum catalytic activity was obtained when the loading ratio was 0.7 and maximum conversion in transesterification was achieved after 2 h when operating parameters are set at 70 ^oC, 6:1 methanol to oil molar ratio with catalyst 0.01 wt.% of oil. After 6 cycles, the catalytic activity decreased marginally but activity was regained after calcination.

Benjapornkulaphong *et al.* [54] investigated and compared the catalytic performance of Al_2O_3-supported alkali, alkali earth metal oxides and effect of calcination temperature on activity of different catalyst for transesterification of palm kernel oil and crude coconut oil with methanol. They found that $Ca(NO_3)_2/Al_2O_3$ calcined at 450 ^oC was the most suitable catalyst giving 94.3% conversion, however when the calcination temperature was increased, the methyl ester formation dropped due to the formation of inactive metal aluminates. On the other hand $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 improved methyl ester formation tendency at the calcination temperature of above 550 ^oC but $LiNO_3/Al_2O_3$ catalyst was active with conversion of 91.6% at 450 ^oC calcination and 93.4% at 550 ^oC. $Mg(NO_3)_2/Al_2O_3$ catalyst was not active at any calcination temperature (only conversion 10.4% at 450 ^oC). After 3 h of reaction time, at 60 ^oC with 65:1 molar ratio of alcohol/oil and 10 wt.% catalyst content, the maximum conversion reached to 94.3% from palm kernel oil whereas only 85% conversion was obtained in the case of crude coconut oil due to high acid value and moisture content of crude coconut oil than palm kernel oil. But when catalyst amount was increased from 15 to 20 wt.%, the conversion of crude coconut oil also increased from 94% to 99.8%.
Guo *et al.* [55] examined the use of calcined sodium silicate as a novel solid base catalyst in the transesterification of soybean oil with methanol. It was found that a yield of almost 100% biodiesel was achieved using methanol to oil molar ratio of 7.5:1 and 3 wt.% of sodium silicate at 60 °C in 60 min. The catalyst can be reused for at least 5 cycles without loss of activity.

Akbar *et al.* [56] developed a new solid catalyst, Na/SiO_2, for transesterification of Jatropha oil with methanol to produce biodiesel. Na/SiO_2 with a loading of 50:50 molar ratio of Na/Si calcined at 600 ^oC exhibited the best catalytic activity for the reaction. The conversion of vegetable oil is found to be 99%. The optimum reaction conditions are achieved at the reflux temperature of methanol (65 ^oC), with a 15:1 molar ratio of methanol to oil and a catalyst amount of 6 wt.%. The catalyst showed high activity under mild conditions and at a relatively short reaction time of 45 min.

Georgogianni *et al.* [57] tested Mg MCM-41, Mg-Al hydrotalcite and K^+ impregnated zirconia catalysts and found that Mg-Al hydrotalcite was more active catalyst for transesterification of rapeseed oil to biodiesel. Mg-Al hydrotalcite showed particularly the highest activity with conversion reaching 97%. MCM-41 also gave high yields (87%) of methyl esters in the transesterification reaction. Authors also compared these results with that of homogenous catalyst (NaOH) in the transesterification reaction under identical reaction conditions and found that the homogenous catalyst accelerated the transesterification reaction significantly and gave the equivalent conversion only within 15 min.

Sree *et al*. [58] demonstrated transesterification of both edible and non-edible oils using Mg/Zr catalyst (catalyst ratio 2:1 wt/wt.%). The transesterification reaction was carried out at 65 ^oC with 53:1 molar ratio of methanol to oil and a catalyst (0.1 wt.% of oil). The conversion of about 98% was achieved in 50 min. Insignificant decrease of yield up to 5% was observed during transesterification of sunflower oil after fourth cycle. However, the high transesterification activity of Mg/Zr catalyst might be due to the presence of higher number of total basic sites. Total basicity of catalyst was 1204 μmol/g while surface area was 47 m^2/g.

Samart *et al*. [59] demonstrated that KI supported on mesoporous silica can be used to catalyze transesterification of soybean oil using methanol for biodiesel production with the conversion close to the conventional methods. The optimum condition was the reaction temperature at 70 ^oC, 15 wt.% of KI, a reaction time of 8 h., and a catalyst amount of 5% by weight of the oil which yielded 90% conversion. The result shows that KI/mesoporous silica is a challenging heterogeneous catalyst for biodiesel production.

Liu *et al.* [23] studied calcium ethoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol and ethanol. The experimental results showed that the optimum conditions are a 12:1 molar ratio of methanol to oil, the addition of 3% $Ca(OCH_2CH_3)_2$ catalyst, and a 65 ^oC reaction temperature. A 95% biodiesel yield was obtained within 1.5 h in these conditions. It also indicated that the catalytic activity of calcium ethoxide is better than that of CaO. Besides, a 91.8% biodiesel yield was obtained when it catalyzed soybean oil to biodiesel with ethanol at 75 ^oC in 3 h.

Liu *et al*. [60] also studied calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. The experimental results show calcium methoxide has excellent catalytic activity and stability in the transesterification of soybean oil to biodiesel with methanol, and the optimal conditions are: 1:1 volume ratio of methanol to oil, addition of 2 wt.% $Ca(OCH_3)_2$ catalyst, 65 ^oC and about 2 h of reaction time and yield of biodiesel obtained was 98%. Besides, the recycling experiment results showed it had a long catalyst lifetime and could maintain activity even after being reused for 20 cycles.

Nd_2O_3 loaded with KOH showed high catalytic activities for the transesterification reaction [61]. Both the K_2O species formed by the thermal decomposition of loaded KOH, and the surface K-O-Nd groups formed by salt-support interactions, were probably the main reasons for the catalytic activity towards the reaction. The catalyst with 30 wt.% KOH loading on Nd_2O_3 and calcined at 600 ^oC for 12 h was found to be the optimum catalyst, which gave the best catalytic activity. When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to oil of 14:1, a reaction time 1.5 h, a reaction temperature 60 ^oC and a catalyst amount 6 wt.% of oil, the highest biodiesel yield reached 92.41%.

CONCLUSION

Biodiesel is an alternative and renewable fuel for diesel engines and has become more attractive in recent times. The catalysts used in the production of biodiesel are acids, bases and enzymes. From this review, it is learnt that the importance of heterogeneous base catalyst for biodiesel production is growing as heterogeneous base catalysts are more effective than heterogeneous acid catalysts and enzymes. Hence, researchers should concentrate for the development of economically viable as well as ecofriendly heterogeneous catalysts for biodiesel production.

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