The effects of catalysts in biodiesel production: A review

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Review

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1. Introduction

Energy is the prime mover for socio-economic development. The World’s economic growth is affected by climatic change, fuel price hike, and the gradual depletion of fossil fuel reserves. Therefore, to increase energy security for economic development, the need to search for an alternative source of energy such as biodiesel is necessary [1,2]. Biodiesel is renewable, sustainable, biodegradable, and emits low greenhouse gases [3,4]. As well, the oxygen content of 11–15% in the molecular structure speed up the combustion process in compression ignition engines and decreases pollutants such as soot, fine particles, and carbon monoxide (CO)
Thus, biodiesel is a potential substitute to replace/supplement petro-diesel fuel [7,8].

Biodiesel fuel is produced via transesterification of refined vegetable oil, waste cooking oil, and used frying oil using alkaline catalysts [9-12] as shown in Fig. 1. The nature of catalyst employed during transesterification reaction is crucial in converting triglycerides to biodiesel. As a result different catalysts have been explored for converting triglycerides to biodiesel fuel. The catalysts usually employed to catalyze transesterification reaction are homogeneous catalysts and heterogeneous catalysts. Conventionally, homogeneous alkaline catalysts such as NaOH, KOH, CH₃ONa, and CH₃OK are more often used in producing biodiesel [13]. The catalytic performance of these catalysts and their ability to perform under moderate conditions has led to their choice [14]. Among these homogeneous alkaline catalysts, CH₃ONa is most active, providing biodiesel yield above 98 wt% in short reaction time (30 min) [15,16]. However because of low price, industrial biodiesel production process mostly employs NaOH and KOH [14].

The process involving these catalysts needs high-quality feedstocks and the free fatty acids (FFAs) level of the feedstocks should not exceed 3 wt%, beyond which the reaction will not occur. In addition, water content of the feedstocks is critical, as a result the feedstocks used in alkali-catalyzed transesterification have to anhydrous [14,17]. Thus, presence of water leads to hydrolysis of oils to FFAs. Fig. 2 shows water hydrolysis of fats and oils to form free fatty acid. The FFAs react with alkaline catalysts to produce soaps formation. Fig. 3 presents soaps formation in homogeneous alkali-catalyzed transesterification. Soaps formation consumes the catalyst, deactivates it and makes biodiesel purification process difficult [13,18]. Therefore, preparation of biodiesel by low quality feedstocks containing high quantity of FFAs and water needs sound technology [19]. However, high cost of refined feedstocks result in high price of biodiesel compared to diesel fuel [15,20].

The cost of refined feedstocks, account to over 70% of the overall cost of biodiesel production [21]. As a result, different kinds of low quality feedstocks such as: waste cooking oils, used cooking oil, greases (yellow and brown), and non-edible oils have been investigated [12-22]. The price of low quality feedstocks such as waste cooking oils is 2-3 times lower than refined oils. Nonetheless, the feedstocks contain higher amount of FFAs and water contents. This features makes their processing challenging [23,24]. Therefore to augment their processing difficulties, acid-catalyzed transesterification is first employed to decrease the content of FFAs before performing alkali-catalyzed transesterification [19]. Thus adopting two-step transesterification technique could provide large biodiesel conversion of up to 98% [25].

Recently heterogeneous catalysts such as solid catalysts and enzyme catalysts are employed to catalyze transesterification reaction for producing biodiesel. Heterogeneous catalysts offer many advantages over homogeneous catalysts such as: simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, less added cost of purification, and simple glycerol recovery. Besides, most of the heterogeneous catalysts used especially solid alkaline catalysts have provided high yields [26], though faced with problems such as extractability [27]. Also, the stability of enzymes catalysts in non-aqueous media is significant to its excellent catalytic activity, this improves transesterification and esterification during biodiesel production [28] and providing high biodiesel yield (95 wt%) [29]. However, the problem mostly associated with enzymes catalysts is the cost of the enzymes, but immobilization of the catalyst could mitigate the cost [30]. Therefore, to achieve biodiesel that is economically feasible, development of active and cheap catalysts for effective transesterification of different kinds of feedstocks is necessary [31]. In this regards, this study extensively examined and reported the effects of different catalysts in producing biodiesel fuel.

2. Biodiesel production

2.1. Techniques for biodiesel production

Biodiesel is usually produced through different techniques such as direct/blends [32,33], microemulsion [34,35], pyrolysis [36,37] and transesterification [38,39]. As stated earlier, alkali-catalyzed transesterification is the most adopted technique for producing biodiesel, this method usually needs refined feedstocks containing less FFAs content otherwise it will result to much soaps formation. For alkali-catalyzed transesterification, if the feedstocks contains high amount of FFAs then it has undergo pretreatment steps before transesterification [40]. Hideki et al. [14] and Ramadhas et al. [25] recommended acid value of feedstocks to be less than 4.0 mg KOH/g before performing alkaline transesterification. Although, Canakci and Gepen [41] and Mittelbach [42] stated that before alkali-catalyzed transesterification, the acid value of a feedstock has to be 2.0 mg KOH/g. Nonetheless, the use of heterogeneous catalysts in biodiesel production has reduced the effects of using low quality feedstocks, especially enzymes catalysts that has the potential of converting FFAs into biodiesel, besides high purity by-products [14].

2.2. Feedstocks for biodiesel production

Biodiesel production is achieved via different kinds of feedstocks. The nature of feedstock used is dependent on the geographical position and climate of the place. For instance Europe employs sunflower and rapeseed oils, palm oil from tropical countries, soybean in United States and canola oil in Canada [43]. Singh and Singh [44] reported the major feedstocks employed in producing biodiesel are cotton seed, palm oil, sunflower, soybean, canola, rapeseed, and Jatropha curcas.
Additionally, Zhang et al. [45] remarked that employing feedstocks such as waste frying oils, non-edible oils, and animal fats, as feedstocks could be useful in producing biodiesel. Although, Baneje and Chakraborty [46] stated that FAs contents in the waste cooking oil should be kept within certain limit for reaction involving both acid- and alkali-catalyzed transesterification reactions. Otherwise these substances may cause severe difficulties in refining of biodiesel products. Table 1 presents the recommended FAs values for alkali-catalyzed transesterification method. While Table 2 shows FAs contents of different vegetable oils. In addition, Table 3 presents FAs levels of most of the feedstocks used to produce biodiesel. The cost of feedstocks decreases as FAs content increases. In case of industrial biodiesel production, there is need for low-cost (high FFA) Feedstocks such as used cooking oils, waste cooking oils, and non-edible vegetable oils. Since biodiesel fuels from refined oils are costly when compared to petro-diesel fuel. Besides, the application of such feedstocks in biodiesel production could minimize competition between demand of edible vegetable oils and cost of biofuel [27]. In addition, application of vegetable oils as sources of biodiesel needs great efforts to either develop more productive plant species with a high yield of oil or to increase oils’ production [72].

Further, many studies have reported microalgae oil as feedstocks for producing biodiesel [73-78]. Demirbas [79] noted that microalgal oil is the only feedstock that can meet the global demand for transport fuels. The author also reported that soon, microalgal oil will become the most important feedstocks for biofuel production. Singh and Gu [80] reported that microalgae feedstocks are receiving great attention as sources of energy because of their quick growth potential coupled with reasonably high lipid, carbohydrate and nutrients contents. In addition, Demirbas [81] highlighted that microalgae possess much quicker growth-rates than terrestrial crops. The author noted the per unit area yield of oil from algae is estimated to be from 20,000 to 80,000 l per acre, per year. In deed this is 7–31 times more than the next best crop, palm oil. Table 4 presents lipid content in the dry biomass of various species of microalgae [82].
Also to highlight the significance of microalgae as feedstock for biodiesel production, Tran et al. [83] have reviewed biodiesel production via microalgae oil. The authors noted that catalysts such as acid, base, and zeolites catalysts can be used in catalyzing transesterification involving microalgae oil as feedstocks.

3. The effects of homogeneous catalyst in biodiesel production

3.1. The effects of alkaline catalysts in biodiesel production

Application of alkali-catalyzed transesterification reaction provide faster rate, nearly 4000 times faster than that catalyzed by the same amount of an acid catalyst [14]. Some of the alkaline catalysts used for the transesterification reaction include among others; NaOH [19,84], KOH [85,86], and sodium methoxide [16,84]. Other alkaline catalysts include; sodium ethoxide [57], potassium methoxide [3,13], sodium propoxide [57], sodium butoxide [31] and carbonates [31,87], etc. Based on biodiesel yield, CH₃ONa or CH₃OK are better and more suitable catalyst than NaOH and KOH. Thus, CH₃ONa and CH₃OK are more suitable due to their ability to dissociate into CH₃O⁻ and Na⁺ and CH₃O⁻ and K⁺ respectively. Besides, the catalysts do not form water during transesterification reaction [3]. For these reason, alkaline catalyst is mostly preferred in commercial production of biodiesel fuel [13]. Transesterification of refined oils with less than 0.5 wt% FFAs via chemical catalysts could lead to high-quality biodiesel fuel with better yield within short time of 30–60 min [88]. Fig. 4 presents the mechanism of base-catalyzed transesterification reaction [71]. Vicente et al. [89] have compared different basic catalysts (sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide) to produce biodiesel fuel using sunflower oil. The reactions were conducted at temperature of 65 °C, methanol to oil molar ratio of 6:1 and basic catalyst by weight of vegetable oil of 1%. They achieved 85.9 and 91.67 wt% yield of esters for NaOH and KOH and 99.33 and 98.46 wt% yields of esters for CH₃ONa and CH₃OK respectively. The authors recorded 98 wt% yields of esters for methoxide after separation and purification steps were completed. Further, less yields losses and negligible ester dissolution in glycerol were observed with methoxide compared to hydroxides. Umer et al. [90] used alkali catalyst to produce sunflower oil methyl esters. They reported notable yield of 97.1 wt% at 60 °C. In addition, alkaline catalysts concentrations ranging from 0.5–1 wt% could yield 94–99 wt% conversion of vegetable oils to alkyl esters. However, increase in catalyst concentration above 1 wt% does not increase the conversion but could add to extra costs of production. Since it is essential to get rid of the catalyst from the products after the reaction is completed [91,92].

Chung [93] transesterified V. fordii and C. japonica seed oils with methanol using alkaline catalysts (KOH, NaOH, and CH₃ONa) to produce biodiesel. The authors noted that KOH provided higher catalytic activity to the seed oils in the reaction. The optimum reaction conditions used were: 6:1 molar ratio of methanol to the seed oils, 1 wt% loading amount of catalyst, 65 °C reaction temperature, and reaction time of 3 h. The biodiesel contents of the C. japonica and V. fordii seed oils under these reaction conditions were 97.7% and 96.1% on KOH catalyst. Figs. 5 and 6 shows the effects of alkaline catalysts on feedstocks contain high amount of water and FFAs [94]. The lesser the water and FFAs contents the better yield vice versa. In another study, Sahoo et al. [48] employed alkaline transesterification after reducing the FFAs value from 44 mg KOH/g a below 4 mg KOH/g through acid catalyzed transesterification. The author found that 1.5 wt% of KOH was adequate to obtained maximum biodiesel yield. Marchetti and Errazu [95] revealed that ethanol and sulfuric acid are suitable to carry out both direct esterification and transesterification reactions simultaneously. These processes could
Fig. 5. Graph of methyl esters yield against water content in transesterification reaction.

Fig. 6. Graph of methyl esters yield against FFA in transesterification reaction.

effectively convert waste cooking oil containing high amount of FFAs ranging from 3% to 40% to biodiesel. The authors noted the FFAs content was reduced via esterification process from 10.684% to a value close to 0.54 wt%. Though, the final FFAs concentration was slightly more than the recommendable quantity. They reported minimized soaps formation during alkali-catalyzed transesterification reaction.

Further, to improve biodiesel production process, Refaat et al. [96] studied microwave irradiation technique to produce biodiesel. They employed sunflower oil (used 3 times at a cooking temperature of 130 °C) and methanol to oil ratio of 6:1 in the presence of 1 wt% of potassium hydroxide at 65 °C. The authors used a normal pressure glass reactor 500 ml flask and reflux condenser. Using the microwave system, the vegetable oil was preheated to a desired temperature of 65 °C. The mixture of alcohol and catalyst then charged into the flask through the condenser. The power output adjusted to 500 W and under reflux the mixture irradiated via different reaction times of 0.5, 1, 1.5, 2, 2.5, 3 and 6 min. Using microwave irradiation technique, reaction time was reduced by 97% and the separation time reduced by 94%. They recorded biodiesel yield of 100% within 2 min and separation time of 30 min. Also, Sufiuddin and Chua [97] optimized transesterification of used frying oil to ethyl ester using microwave irradiation. They used a microwave oven equipped with non-contact infrared continuous feedback temperature system and magnetic stirrer to heat the oil and the alcohol at 60 °C. Twenty five percent (25%) of an exit power of 750 W was used to irradiate the reaction mixture. The authors experimented different concentrations of sodium methoxide (0.3 wt% to 0.5 wt%) and achieved maximum conversion (87 wt%) at 0.5 wt%. During transesterification process, both sodium ethoxide and potassium hydroxide provided good conversions. However, due simplicity in products phase separation, sodium ethoxide was viewed as most promising catalyst for producing biodiesel. Besides, microwave-assisted transesterification process dramatically reduced the reaction time from 75 min to 4 min at 60 °C, thus saving great time. Additionally during transesterification, irradiation times must be controlled and the levels of radiation power should not be too high, to avoid destruction of organic molecules.

Moreover, to determine optimum operating parameters such as catalyst concentration, Ferrera et al. [98] studied transesterification reaction of rapeseed oil for biodiesel production using response surface methodology (RSM). They employed a 500 ml jacketed stirred (at 600 rpm) reactor tank. At optimum conditions of temperature of 50 °C, KOH concentration of 0.6% (w/w), reaction time of 90 min, and 60 methanol to KOH ratio by weight, large amount of triglycerides, diglycerides and monoglycerides were converted into biodiesel. As well, the final concentrations were 0.05% triglycerides, 0.09% diglycerides and 0.36% monoglycerides and the triglyceride conversion was 98–99%.

The effects of catalysts such as NaOH on transesterification of rapeseed oil under supercritical/subcritical conditions were also studied by He et al. [99]. The authors employed little quantity of NaOH as catalyst and achieved excellent biodiesel yield with no soaps formation.

3.2. The effects of acid catalysts in biodiesel production

The most notable acids commonly employed in transesterification reaction include among others; sulfuric acid [11,19,100], sulfonic acid [14], hydrochloric acid [16], organic sulfonic acid [14], ferric sulfate [13], etc. Among these acids, hydrochloric acid, sulfonic acid and sulfuric acid are usually favored as catalysts for the production of biodiesel. The catalyst and the alcohol are vigorously mixed with a stirrer in a small reactor. The oil is first charged into the biodiesel reactor and then the mixture of catalyst/alcohol is fed into the oil. Bremset acids preferably sulfuric acid or sulfonic acid is used to catalyze the reaction. Although the catalysts give high yield of biodiesel, but the reaction rates are slow. The alcohol to oil molar ratio is the main factor influencing the reaction. Therefore addition of excess alcohol speeds up the reaction and favors the formation biodiesel products. The steps involve during acid-catalyzed transesterification are: (1) initial protonation of the acid to give an oxonium ion (2) the oxonium ion and an alcohol undergo an exchange reaction to give the intermediate (3) and this in turn can lose a proton to become an ester. Reversibility of each of the above step is possible but the equilibrium point of the reaction is displaced in the presence of excess large alcohol, by allowing esterification to advance to completion [16]. Leung et al. [40] reported that esterification by acid-catalysis makes the best use of the FFAs in the animal fats and vegetable oils and converts them into fatty acid alkyl esters. The authors noted that one-step esterification pretreatment may not reduce the FFAs efficiently, if the acid value of the oils or fats is very high. This is because of the high content of water produced during the reaction. In this case, addition of
Table 5  
Reaction yield as a function of the homogeneous catalyst weight.

<table>
<thead>
<tr>
<th>Feedstock (oil)</th>
<th>Catalyst</th>
<th>Conc. (wt/v)</th>
<th>Reaction time (h)</th>
<th>Reaction temp (°C)</th>
<th>Yield/conv. (wt/wt%)</th>
<th>Molar ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste tallow (chicken)</td>
<td>H₂SO₄</td>
<td>1.25</td>
<td>24</td>
<td>50</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[85]</td>
</tr>
<tr>
<td>Palm fatty acid</td>
<td>H₂SO₄</td>
<td>2</td>
<td>70</td>
<td>96</td>
<td>99.6 ± 0.01</td>
<td>7:2:1</td>
<td>[9]</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>KOH</td>
<td>0.5</td>
<td>70</td>
<td>96</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[104]</td>
</tr>
<tr>
<td>Jatropha oil-wax</td>
<td>Sodium methoxide</td>
<td>0.5</td>
<td>10</td>
<td>55</td>
<td>98.27 ± 0.01</td>
<td>7:5:1</td>
<td>[105]</td>
</tr>
<tr>
<td>Canola oil</td>
<td>KOH</td>
<td>0.5</td>
<td>1</td>
<td>92</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[107]</td>
</tr>
<tr>
<td>Jatropha carcas</td>
<td>KOH</td>
<td>1</td>
<td>1</td>
<td>92</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[108]</td>
</tr>
<tr>
<td>Cottonseed oils</td>
<td>Sodium hydroxide</td>
<td>0.5</td>
<td>1</td>
<td>77</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[109]</td>
</tr>
<tr>
<td>Roselle oil</td>
<td>Potassium hydroxide</td>
<td>1.5</td>
<td>60</td>
<td>94.4 ± 0.01</td>
<td>94.4 ± 0.01</td>
<td>1:30</td>
<td>[110]</td>
</tr>
<tr>
<td>Rubber seed oil</td>
<td>NaOH</td>
<td>1</td>
<td>1</td>
<td>92</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[111]</td>
</tr>
<tr>
<td>Mahua oil (Madhaca indica)</td>
<td>NaOH</td>
<td>1</td>
<td>2</td>
<td>88.9 ± 0.01</td>
<td>88.9 ± 0.01</td>
<td>1:30</td>
<td>[63]</td>
</tr>
<tr>
<td>Mahua oil</td>
<td>H₂SO₄-KOH</td>
<td>1.87</td>
<td>1</td>
<td>98</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[64]</td>
</tr>
<tr>
<td>Sunflower frying oil</td>
<td>KOH</td>
<td>1</td>
<td>0.5</td>
<td>61</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[112]</td>
</tr>
<tr>
<td>Tobacco seed oil</td>
<td>NaOH</td>
<td>1.5</td>
<td>1.5</td>
<td>98</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[113]</td>
</tr>
<tr>
<td>Rice bran oil</td>
<td>Sulfuric acid</td>
<td>2</td>
<td>8</td>
<td>98</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[21]</td>
</tr>
<tr>
<td>Used frying oil</td>
<td>KOH</td>
<td>1</td>
<td>2</td>
<td>72.5 ± 0.01</td>
<td>72.5 ± 0.01</td>
<td>1:30</td>
<td>[12]</td>
</tr>
<tr>
<td>Waste cooking oils</td>
<td>KOH</td>
<td>0.75</td>
<td>0.33–2</td>
<td>90</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[11]</td>
</tr>
<tr>
<td>Jatropha oil</td>
<td>H₂SO₄-KOH</td>
<td>1.5–2.5</td>
<td>0.5–2</td>
<td>90–95</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[114]</td>
</tr>
<tr>
<td>Karanja oil</td>
<td>KOH</td>
<td>1</td>
<td>3</td>
<td>97–98</td>
<td>99.01 ± 0.01</td>
<td>1:30</td>
<td>[115]</td>
</tr>
</tbody>
</table>

mixture of alcohol and sulfuric acid into the oils or fats three times (three-step pre-esterification) is required. The time needed for this process is about 2 h and removal of water is necessary by a separation funnel before adding the mixture into the oils or fats for esterification again. Further, Palliganai and Briggs [24] reported sulfuric acid catalyzed transesterification to provide a few advantages over base-catalyzed technique such as one-step process as opposed to a two-step transesterification. The authors also reported that feedstock with high FFAs content could be easily handle, downstream separation is straightforward, and a high-quality glycerol byproduct is achievable.

Additionally, Soriano Jr. et al. [101] studied transesterification of canola oil to produce biodiesel via homogeneous Lewis acids (AlCl₃) and ZnCl₂ as catalyst. The reaction occurred in a round bottom flask submerged in an oil bath equipped with a reflux condenser, thermometer control and a magnetic stirrer. The authors reported use of variable parameters such as: reaction time (6, 18, 24 h), methanol to oil molar ratio (6, 12, 24, 42 and 80), reaction temperature (75, 110 °C). And tetrahydrofurran (THF) as co-solvent (1:1 methanol to THF by weight in runs with THF), and catalyst (AlCl₃) or ZnCl₂. In all the runs, the catalyst amount was kept at 5% based on the weight of oil, 1H NMR monitored converting canola oil into fatty acid methyl esters. Thus, the best conditions with AlCl₃ were 24:1 molar ratio at 110 °C and 18 h reaction time with THF as co-solvent provided a conversion of 98%. AlCl₃ was far more active compared to ZnCl₂ due to its higher acidity. In another study, Cardoso et al. [102] discussed the effects of Lewis acid on the transesterification process in producing biodiesel. The authors have introduced an inexpensive Lewis acid Ti(N)(B) chloride dihydrate (SnCl₄-2H₂O), and evaluated its potential as catalyst on the ethanalysis of oleic acid of fats and vegetable oils. The catalytic tests were carried out in triplicate with a molar ratio fatty acid: catalyst (100:1), reaction time of 2 h. Using these conditions, the process provided more than 90% biodiesel yield with a high selectivity of more than 93%.

3.3. The effects of homogeneous catalysts on the yield of biodiesel fuel

The nature of catalyst used plays a great role during transformation of vegetable oil to biodiesel [103]. As a result, catalyst is among the key factors determining the rate and yield of biodiesel during biodiesel production process [17,46]. Thus, Table 5 presents reaction yield as function of the homogeneous catalyst weight. The data obtained shows that production of biodiesel via homogeneous catalyst could yield more than 95%.

4. The effects of heterogeneous catalysts in biodiesel production

Despite the problems surrounding alkali-catalyzed transesterification, the process is still favorable in producing biodiesel fuel. The main reason is due to their faster kinetic rate and economic viability [116]. Recently several researches were conducted on heterogeneous catalysts with the aim of finding solutions to problems caused by using homogeneous catalysts in producing biodiesel. As a result a good number of heterogeneous catalysts were explored and many of the catalysts have displayed very good catalytic performances [27]. Some of these catalysts include among others: oxides [117], hydroxides [118], zeolites [119] etc. Currently, majority of heterogeneous catalysts used in producing biodiesel are either oxides of alkali or oxides of alkaline earth metals supported over large surface area [15]. Further, biodiesel is commercially produced using heterogeneous catalyst through the Esterification-H process. This biodiesel process is commercialized by Axens. The process needs neither catalyst recovery nor aqueous treatment steps, which are main bottlenecks from the current homogeneous catalytic processes. Additionally the Esterlip-H process displays high biodiesel yields and directly produces salt-free glycerol at purities exceeding 98% compared to 80% glycerol purity from homogeneous catalyzed process [120].

Thus, the effects of these catalysts are discussed as follows.

4.1. The effects of solid alkaline and acid catalysts in biodiesel production

Sernwal et al. [121] reported that many studies on solid acidic catalysts for producing biodiesel were carried out, however lower reaction rates and unfavorable side reactions have limited their uses. The authors noted that a good number of investigations on basic heterogeneous catalysts were also conducted but their activity gets degraded in the presence of water. They stated that acid–base catalysts are among the most promising catalysts to employ in biodiesel production; this is because they can catalyze both esterification and transesterification simultaneously. Further, Lee and Shiro [122] reported simultaneous esterification and transesterification of waste cooking oil using solid catalyst ZnO-La₂O₃, which combines acid (ZnO) and base sites (La₂O₃). Although the process provided high conversion of 96% in 3 h, but like zirconia, lanthanum is a rare and expensive metal, therefore cost of the catalyst would prohibit it high use in the production of biodiesel. Further gelular resin catalysts having covalently bound