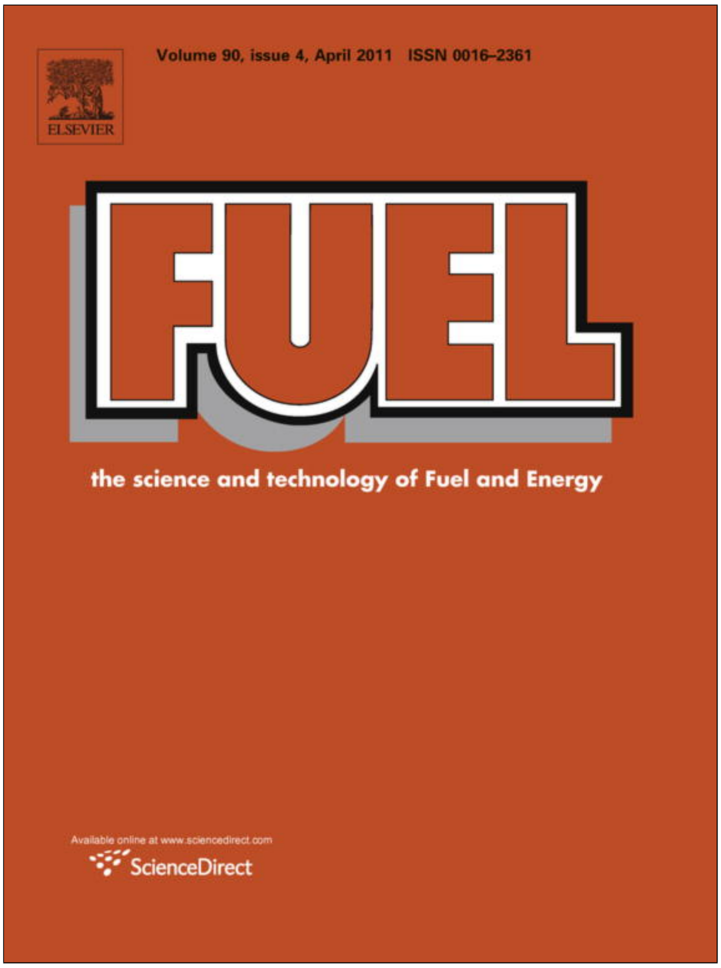
Volume 90, issue 4, April 2011 ISSN 0016-2361
ELSEVIER
FUEL
the science and technology of Fuel and Energy
Available online at www.sciencedirect.com
ScienceDirect

Fuel 90 (2011) 1309–1324

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Review article

# Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review

Yogesh C. Sharma[a,*], Bhaskar Singh[a], John Korstad[b]

[a] *Department of Applied Chemistry Institute of Technology, Banaras Hindu University, Varanasi 221 005, India*
[b] *Department of Biology and Renewable Energy, Oral Roberts University, 7777 South Lewis, Avenue, Tulsa, OK 74171, United States*

ARTICLE INFO

*Article history:*
Received 15 June 2010
Received in revised form 10 October 2010
Accepted 12 October 2010
Available online 23 October 2010

*Keywords:*
Biodiesel
Heterogeneous catalyst
Yield
Calcination
Combustion

ABSTRACT

Heterogeneous catalysts are now being tried extensively for biodiesel synthesis. These catalysts are poised to play an important role and are perspective catalysts in future for biodiesel production at industrial level. The review deals with a comprehensive list of these heterogeneous catalysts which has been reported recently. The mechanisms of these catalysts in the transesterification reaction have been discussed. The conditions for the reaction and optimized parameters along with preparation of the catalyst, and their leaching aspects are discussed. The heterogeneous basic catalyst discussed in the review includes oxides of magnesium and calcium; hydrotalcite/layered double hydroxide; alumina; and zeolites. Yield and conversion of biodiesel obtained from the triglycerides with various heterogeneous catalysts have been studied.

**Contents**

1. Introduction . . . . . 1309
2. Oxides as catalyst. . . . . 1310
    2.1. Oxides of magnesium and calcium . . . . . 1310
    2.2. Strontium oxide as catalyst . . . . . 1314
    2.3. Mixed oxides as catalysts . . . . . 1315
3. Hydrotalcite/Layered Double Hydroxide (LDH) derived catalysts . . . . . 1316
4. Solid superbase catalyst. . . . . 1319
5. Alumina loaded with various compounds as catalyst . . . . . 1319
6. Zeolites as catalyst. . . . . 1321
7. Biodiesel synthesis by supercritical process. . . . . 1321
8. Conclusion . . . . . 1322
Acknowledgements . . . . . 1322
Appendix A. Supplementary data . . . . . 1322
References . . . . . 1322

## 1. Introduction

An impetus in development of renewable sources of energy has resulted in biodiesel development from raw materials such as vegetable and waste cooking oils. Biodiesel is synthesized by reaction of triglycerides with alcohol in the transesterification reaction. The commonly used alcohol is methanol due to low cost and the biodiesel is thus fatty acid methyl ester (FAME). New generation biodiesel intends to derive raw material from algae and other feedstock which will provide sustainability to the energy sources needed to adequately supplement the biodiesel industry. The process that is being adopted worldwide for biodiesel synthesis is transesterification. In the transesterification reaction, the ester group from the triglyceride is detached to form three alkyl ester molecules. The feedstock for biodiesel preparation at industrial level comprises of edible as well as non-edible vegetable oils.

---

* Corresponding author. Tel.: +91 542 6702865; fax: +91 542 2368428.
*E-mail address:* ysharma.apc@itbhu.ac.in (Y.C. Sharma).

0016-2361/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2010.10.015

Irrespective of the feedstock used for biodiesel production, a catalyst is needed to complete the reactions in a considerable time. The only case where catalyst is not needed for biodiesel synthesis is when alcohol and oil are used in supercritical conditions. Though there are recent reports on the use of catalyst even in supercritical conditions.

Catalysts mainly belong to the categories of homogeneous or heterogeneous. Homogeneous catalysts act in the same phase as the reaction mixture, whereas heterogeneous catalysts act in a different phase from the reaction mixture. Being in a different phase, heterogeneous catalysts have the advantage of easy separation and reuse. At present, the biodiesel industry is dominated by application of homogeneous catalysts due to their simple usage and less time required for conversion of oils to their respective esters. The widely used alkaline catalysts NaOH and KOH are easily soluble in methanol, forming sodium and potassium methoxide and augmenting the reaction to completion. When the acid value (AV) of the oil is high, acid catalyst is used to lower the AV and then alkali catalyst is utilized for biodiesel synthesis. Enzymes are the other important catalysts possessing high selectivity and belonging to the homogeneous group of catalysts. However, the constraint that lies with their application for production of biodiesel is their comparatively high cost. Cheaper homogeneous acid and alkali catalysts provide high yield and conversion of biodiesel. However, they need thorough washing by water and neutralization by respective acid or alkali, resulting in the need for extra water and generation of excess wastewater. The biodiesel must then be dried to remove the resultant moisture content. These limitations can be avoided by using a heterogeneous (also called "solid") catalyst. Many of these catalysts have been reported in recent excellent review papers to produce good yield and conversion of feedstock to biodiesel [1–3]. The major drawback of heterogeneous catalysts in general lies their preparation and reaction conditions which is energy intensive which will escalate their production cost and their leaching aspect. For a catalyst to be truly heterogeneous in nature, it should not leach into the reaction medium and should be reused. In addition, the catalyst should have high selectivity for the desired product formation and should give high yield and conversion to biodiesel. The combustion characteristics of the fuel are independent of the catalyst used for transesterification. However, the characteristics of the fuel depend on the feedstock used in synthesis of biodiesel. An overview of which has been discussed in this review. The solid catalysts can be categorized as solid base and solid acid catalyst. Di Serio et al. [2] have discussed the mechanism of various heterogeneous catalysts. Heterogeneous catalysts (acid and base) have been classified as Brønsted or Lewis catalysts. A catalyst may possess one or both of the sites and the relative importance of these two sites is not known so far. The mechanism of reaction for heterogeneous catalysts is similar to that of homogeneous catalysts. In homogeneous catalysts such as sodium hydroxide, potassium hydroxide and sodium methoxide, an alkoxide group is formed on reaction with alcohol, which then attacks the carbonyl carbon atom of the triglyceride molecule. Heterogeneous basic Brønsted and basic Lewis catalysts react similarly with alcohol, forming a homogeneous alkoxide group. The transesterification reaction then occurs between alcohol (usually methanol or ethanol) adsorbed on catalyst and ester of the reactant by the Eley–Rideal mechanism. For acid catalysis, the mechanism is similar for homogeneous and heterogeneous Brønsted and Lewis acid catalysts. Brønsted acid is suitable for esterification reaction, whereas Lewis acid gets deactivated due to the water formed in the esterification and hence is preferred for the transesterification reaction. In homogeneous and heterogeneous Brønsted and Lewis acid catalysts, the reaction mechanism proceeds by protonation of carbonyl group, thus increasing its electrophilicity. This makes the carbonyl group more susceptible to nucleophilic attack. The rate-determining step is different for Brønsted and Lewis solid acid catalyst. For Nafion, a Brønsted solid acid supported on silica, nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol (by Eley–Rideal mechanism) is the rate-determining step. In the case of Lewis acid catalyst, acid strength is the rate-determining step for successful transesterification reaction.

This review paper deals with the solid alkali catalysts used for biodiesel development, the energy input required in the transesterification reaction.

## 2. Oxides as catalyst

Oxides of magnesium and calcium (MgO and CaO) have been tried as solid base catalyst owing to their easy availability, low cost, and non-corrosive nature.

### 2.1. Oxides of magnesium and calcium

Initial research did not show promising results, but later on calcium and magnesium oxides were successfully developed to attain high yield and conversion of biodiesel. When both homogeneous and heterogeneous catalysts were tried for biodiesel development by transesterification of sunflower oil, NaOH (a homogeneous catalyst) performed much better than MgO (a heterogeneous catalyst) in terms of conversion. 100% conversion is reported to have been achieved in 8 h reaction time and 60 °C temperature with NaOH, but only 11% with MgO. Tin chloride, a Lewis acid, gave much lower conversion of 3%. Conversion of vegetable oil to methyl esters obtained with other catalysts such as anion and cation exchange resins, sulphate-doped and silica-doped zirconium hydroxide, titanium silicate, titanium chelate, zeolite, and immobilized lipase were all either 0 or <1% [4]. Lopez [5] also reported only 18% conversion of the feedstock, triacetin after 8 h of reaction time with MgO as catalyst after calcination at 600 °C. The reason attributed is the low surface area of the catalyst. More recently MgO has shown to possess catalytic activity for synthesis of biodiesel. A pioneering wok on catalytic activity of MgO has been reported by Di Serio et al. [6] where 92% yield has been achieved using 12:1 methanol to oil molar ratio, 5.0 wt.% of the catalyst in 1 h. Dossin et al. [7] reported that MgO was found to work efficiently in batch reactor at ambient temperature during the transesterification reaction with production of 500 tonne of biodiesel. As heating is not required during batch process, the overall cost of production of biodiesel is reduced. The kinetic model study has indicated the reaction with MgO to be faster than the conventional base catalyzed transesterification without formation of a byproduct [8]. MgO has shown increase in reaction rate when used in supercritical conditions. Though the reaction get complete in 10 min, a high temperature (300 °C), and a high methanol to oil molar ratio of 39.6:1 was needed to achieve 91% of FAME yield [9].

MgO, when loaded on three different mesoporous silicas (MCM-41, SBA-15, and KIT-6), was found to be quite effective resulting in high conversion. The catalyst was coated by two different methods: in situ coating and impregnation methods. X-ray photoelectron spectroscopy (XPS) showed low attachment of MgO over the surface of SBA-15 catalyst by in situ coating method compared to impregnation method. This resulted in higher surface area and pore volume of the catalyst obtained by in situ route rather than with impregnation method. As more available Mg enhances the transesterification reaction, SBA-15 resulted in better activity with preparation via impregnation method. Since the mechanism of heterogeneous catalysis is adsorption, surface Mg concentration was found to be more dominant over other physical properties such as surface area, pore volume and pore size. Though a high conversion of 96% was obtained, the reaction conditions (220 ° for 5 h in batch reactor with continuous stirring with MgO loaded on SBA-15) were energy intensive which may incur high cost for biodiesel production [10]. KOH loaded on MgO by wet impregnation method has shown high conversion (99.36%) and yield (95.05%) of biodiesel from canola oil. Upon addition of 20 wt.% KOH loaded on MgO, the total basicity increased to 6.0 mmol/g and was observed to be optimum for best performance of the catalyst activity (Fig. 1). K interacts with Mg and weakens the Mg–O bond. This facilitates migration of $O^{2-}$ species that react with the $CO_2$ present in air during calcination. This leads to the formation of $K_2CO_3$ dispersed over magnesia from KOH loading as determined by Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) analysis. $K_2CO_3$ acts as a heterogeneous catalyst. Though the optimum reaction conditions were moderate for molar ratio {i.e. 6:1 (alcohol to oil)} and catalyst amount (3%), a longer reaction time was required (7 h) which will incur high cost of the overall process [11]. Loading $K_2CO_3$ on MgO ($K_2CO_3$/MgO loading ratio 0.7) has shown a high yield of 99.5%. A high base strength of PKa value between 15 and 18.4 (higher than that of $K_2CO_3$) has been attributed to the decomposition of $K_2CO_3$ to $K_2O$ by calcinations. $Al_2O_3$ and CaO, when tried as carriers instead of MgO, have also shown a high yield of 98%. However, $K_2CO_3$/CaO was found to be sensitive to water and was converted to hydroxide. $K_2CO_3$/MgO was resistant to water content; 1% water only reduced the catalytic activity to 95%. The finding is significant in view of the lesser amount of catalyst (1 wt.%) and reaction time (2 h) along with molar ratio {(6:1) alcohol to oil} utilized for transesterification. The catalyst was reused after calcination (at 400 °C for 4 h) for 6 runs and found to be significantly effective (98% yield). The residual potassium content of the product was determined to be less than 1 ppm, showing only minor leaching of the catalyst [12].

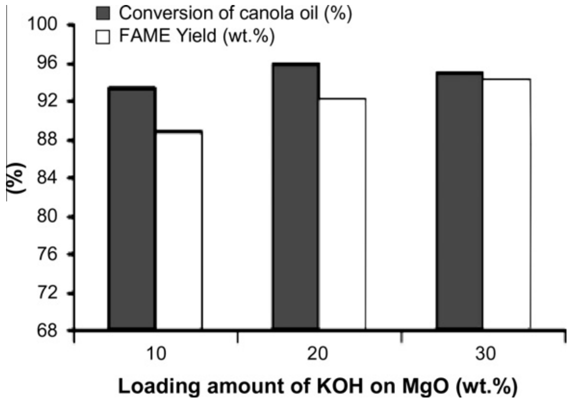

**Fig. 1.** Catalyst, MgO supported KOH [11]. Influence of KOH loading on the conversion and FAME yield. [*Reaction conditions*: Methanol to oil molar ratio, 6:1; catalyst amount, 3.0 wt.%; reaction time, 9 h; temperature, 333 K].

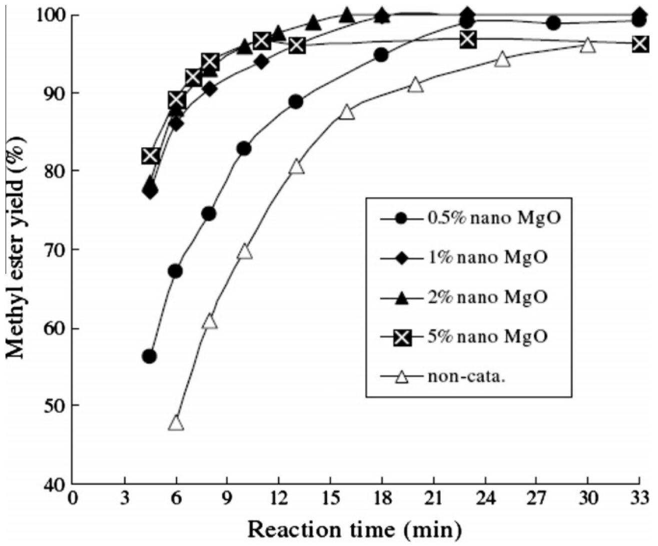

**Fig. 2.** Catalyst, nano-MgO [13]. Effect of nano-MgO content on methyl ester yield from sunflower oil transesterification. [*Reaction conditions*: 250 °C; reaction pressure 24.0 MPa; Methanol to oil molar ratio, 36:1; stirring 1000 rpm].

Reduction in reaction time for transesterification has been brought by using 3.0 wt.% of nano-MgO (60 nm) as catalyst in just 10 min in supercritical or sub critical conditions. However, the process required a high amount of methanol (36:1 M ratio), high temperature (260°C), and pressure (24.0 MPa). The activation energy needed with nano-MgO as catalyst was found to be 75.9 kJ/mol, which is lower than that without MgO (92.5 kJ/mol), which results in shorter reaction time. Yield of methyl esters was low in a non-catalytic system; however, the difference narrowed with reaction time (Fig. 2). It can be seen at even a low amount of catalyst, nano MgO (i.e. 0.5%) was able to effectively catalyze the reaction. Experiments with usual MgO were not attempted, which could have provided a comparison to justify the suitability of nano-size synthesis of MgO as catalyst [13]. Fabrication of the catalyst into macrospherical form instead of the usual powder form resulted in its improved performance. The catalyst has been prepared from γ-$Al_2O_3$ spheres, used as template and $Mg(NO_3)_2{\cdot}6H_2O$ by urea hydrolysis method. γ-$Al_2O_3$ was later removed by treatment with 0.2 M NaOH. Magnesium–aluminum layered double hydroxides were formed, which upon heating and calcination gave the magnesia-rich magnesium aluminate spinal framework, i.e. $MgO{\cdot}MgAl_2O_4$ to be composed of aggregates of rod-like nanoparticles. However, the yield obtained with the catalyst $MgO{\cdot}MgAl_2O_4$ and MgO/$MgAl_2O_4$/γ-$Al_2O_3$ were substantially low at 57% and 36% respectively in 10 h. Higher catalytic activity of the catalyst $MgO{\cdot}MgAl_2O_4$ has been attributed to the increase in its base strength, which resulted from leaching of amphoteric $Al^{3+}$ during the preparation of the catalyst. The specific basicity of $MgO{\cdot}MgAl_2O_4$ was found to be 372 μmol/g and that of MgO/$MgAl_2O_4$/γ-$Al_2O_3$ was 277 μmol/g. The higher specific basicity along with higher surface area, pore volume, pore size, and porous structure of $MgO{\cdot}MgAl_2O_4$ resulted in better diffusion of the reactants and product molecules with the catalyst, thus proving it to be a better catalyst [14]. Hence, even with low yield the study is significant in the sense that basicity of the catalyst may be modified by selective leaching of template. However, literature on nano-size catalysts is not readily available, so research on such catalysts is important owing to their enormous surface area.

Like magnesium oxide, calcium oxide (CaO) as a catalyst has gained attention among researchers worldwide for the development of biodiesel owing to its low cost and easy preparation. However, an important aspect in dealing with calcium oxide as catalyst is its modification by calcination and to oversee its leaching in biodiesel. Also, presence of water and influence of free fatty acid (FFA) have to be considered for its application. Huaping et al. [15] used CaO as heterogeneous catalyst for biodiesel synthesis from *Jatropha curcas* oil. The base strength of calcium oxide increased to 26.5 (grouped in the category of super base) on treatment with ammonium carbonate solution and further calcination. Calcination at 900 °C resulted in 93% conversion of jatropha oil to biodiesel under optimized conditions (70 °C temperature, 2.5 h reaction time, 1.5% catalyst amount, and 9:1 methanol to oil molar ratio). At high calcination temperature, calcium carbonate was decomposed, producing defects in its crystal structure. The defects then favored the formation of calcium methyloxide which is a surface intermediate in the transesterification reaction. The catalyst was further reused three times with 92% conversion of jatropha oil. Even though biodiesel was synthesized, calcium ions were reported to have leached in the biodiesel. Calcium ions, water, oxalic acid, citric acid, and ethylene diamine tetra acetic acid (EDTA) have been used as decalcifying agents. Water washing was not found to be a suitable decalcifying agent, reducing the yield to 69.5%. Among the other decalcifying agents, citric acid gave the best yield of 95.5%, followed by EDTA (92.3%) and oxalic acid (90.7%). Owing to the leaching aspect of calcium ions, the suitability of this catalyst as a heterogeneous one cannot be justified. A study on stability and surface poisoning of calcium oxide when used as catalyst by Granados et al. [16] revealed that the active sites of CaO were poisoned by carbon dioxide ($CO_2$) and atmospheric water ($H_2O$). On 10 days exposure to room air, activated CaO was fully transformed to $Ca(OH)_2$ with no trace of CaO. This could be overcome by activation treatment of the catalyst for removing the carbonate groups, which act as the main poisoning species, and further preventing the catalyst from coming in air contact. Evacuation of the catalyst at 500 °C resulted in improvement of catalytic activity due to dehydration of $Ca(OH)_2$. But, as the catalyst is cooled to room temperature, the surface of CaO gets covered by OH groups. To overcome this, the catalyst is outgassed at 700 °C to revert the $CO_2$ poisoning and the catalyst gets highly activated. It was observed that poisoning occurred more due to carbonation of CaO than hydroxylation. The catalyst has been successfully reused up to 8 times, but dissolution of the catalyst has been reported as it is soluble in methanol to about 0.035 wt.%. The leaching of catalyst was evident from the solution of methanol and CaO (discarding the solid CaO) taken for transesterification reaction. The solution gave yield of 60% indicating the leaching of the catalyst which might discourage its application as a heterogeneous catalyst (Fig. 3) [16]. Calcination temperature of 550 °C was found to be optimum for CaO as catalyst to get rid of the poisoning species (mainly water and carbonate) because $Ca(OH)_2$ is dehydrated at 550 °C. Further increase in calcination temperature to 600–700 °C substantially reduced the yield of methyl esters. The catalyst calcined at 900 °C resulted in 0% yield of biodiesel. This has been attributed to the rearrangement of solid surface and bulk atoms at higher temperature. The chemical reaction was found to follow pseudo-first order reaction kinetics. The triglyceride mass transfer limitation observed initially was overcome by advancement of reaction and increase in catalyst amount [17]. The active phase present in calcium oxide has also been investigated by Kouzu et al. [18]. After completion of the transesterification reaction using calcium oxide as catalyst, the catalyst was collected and analyzed to examine the active phase of calcium oxide. The catalyst was analyzed by various instrumental methods such as XRD, IR spectroscopy, $^{13}C$ NMR, and SEM, and the results showed the catalyst consisted of calcium diglyceroxide. Calcium diglyceroxide was formed by the transesterification reaction of calcium oxide with the by product glycerol and was a major

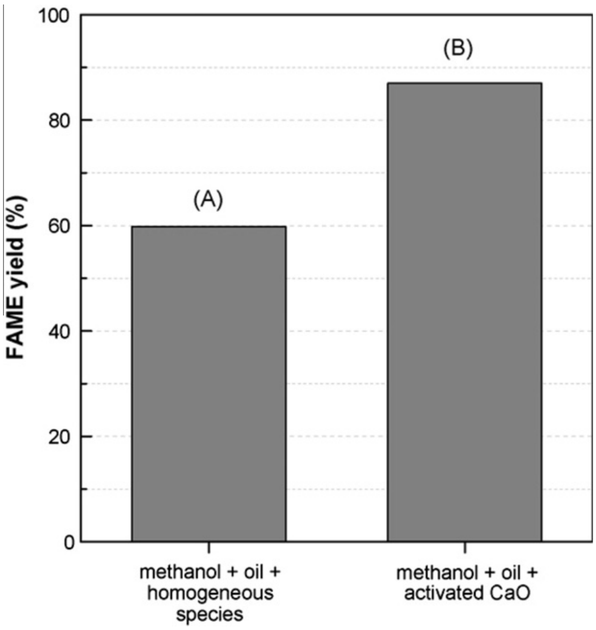

**Fig. 3.** Catalyst, CaO [16]. Yield of FAME obtained by using (A) homogeneous species created by contacting the methanol and the activated CaO for 2 h at 60 °C and (B) by using the activated solid CaO.

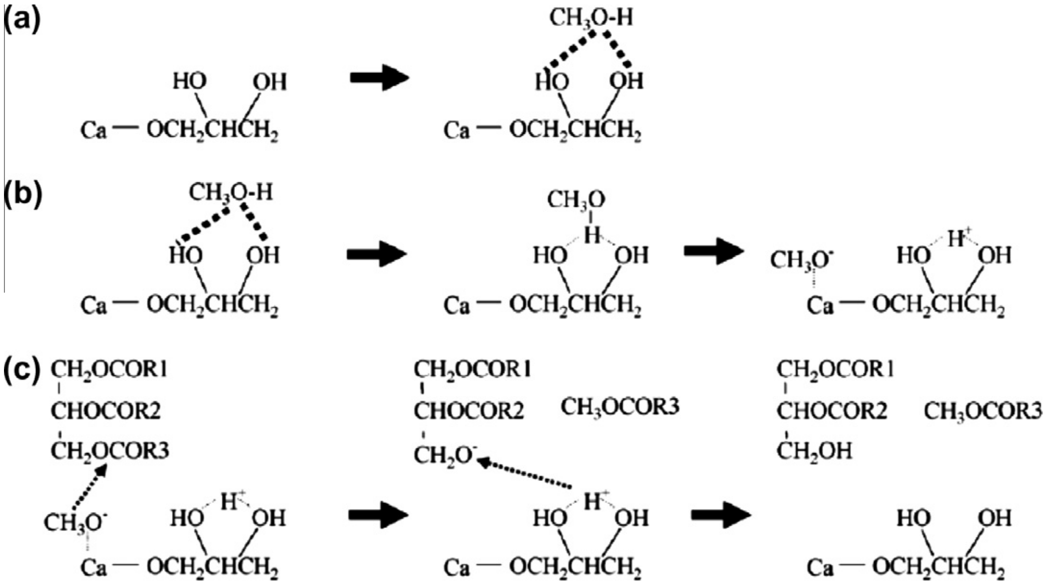

**Fig. 4.** Catalyst, CaO and calcium diglyceroxide [17]. Possible mechanism for transesterification of vegetable oil with methanol catalyzed by calcium diglyceroxide. (a) Adsorption of methanol onto catalyst; (b) abstraction of proton by basic sites; and (c) nucleophilic reaction with methoxide anion followed by stabilization of the anion by proton.

constituent of the collected catalyst. For comparison, calcium diglyceroxide was also prepared by CaO at reflux of methanol with 50% glycerol for 2 h under atmospheric pressure, and the activity of both the catalysts was found to be similar. Absence of calcium methoxide was confirmed by $^{13}C$ NMR. The activity of the collected catalyst was reduced due to decrease in strength of the basic sites. The active site of the used catalyst was thought to be due to OH groups from calcium diglyceroxide. However, the feedstock was low in acid value, which otherwise would have resulted in calcium soap formation. The mechanism of the reaction is shown in Fig. 4a–c. The two OH groups favored the adsorption of methanol-forming hydrogen bonds (Fig. 4a). The OH groups also enhanced the abstraction of protons (Fig. 4b). Calcium methoxide possessed stronger basic sites as compared to calcium diglyceroxide but became poisoned (Fig. 4c). Presence of water up to 1000 ppm promoted the yield of biodiesel. Further increase in moisture up to 2500 ppm showed no further increase in biodiesel yield. The moisture most likely enhanced the mobility of reactants from the surface of the catalyst. Tolerance to moisture (up to 0.25 wt.%) is always an advantage for catalysts used in transesterification reactions where moisture may be entrapped in reactants via feedstock or alcohol. The catalyst, calcium diglyceroxide, was also found to be tolerant to air exposure. When exposed to air for 30 min, the yield was not reduced. Contrary to this, yield of biodiesel decreased substantially when the catalyst, calcium oxide, was exposed to air for 30 min. Yield reduced from 93% to just 10% in 30 min. exposure. Even a 3 min exposure was found to deactivate the catalyst [18]. Liu et al. [19] found that water content of 2.0% showed positive influence on yield of biodiesel using CaO as catalyst. Water molecules are assumed to have been adsorbed on the CaO surface to form OH groups, which provided active basic sites for transesterification and enhanced the reaction rate. Ninety five percent yield was achieved with a 12:1 alcohol to oil molar ratio with 2.0% water dissolved in methanol at 65 °C. However, water content over 2.80 wt.% of the oil will hydrolyze the ester formed and will result in saponification. The catalyst was reused for 20 runs with just a slight decrease in biodiesel yield (Fig. 5).

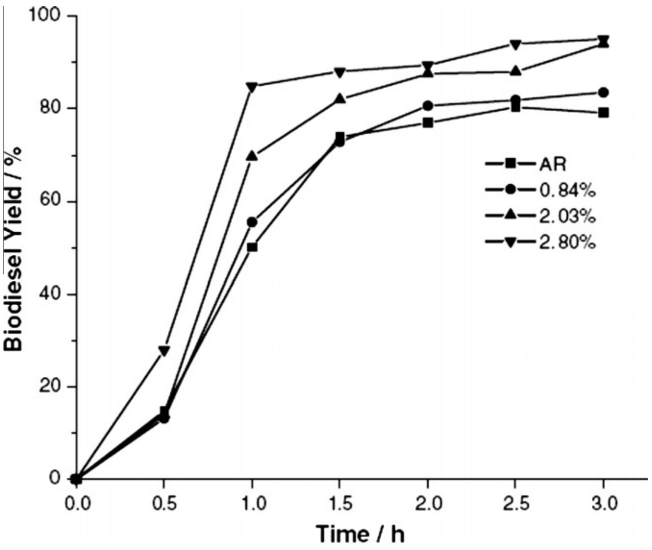

**Fig. 5.** Catalyst, CaO [19]. Effect of water content of methanol on biodiesel yield. [*Reaction conditions*: CaO to oil mass ratio, 8%; methanol to oil molar ratio, 6:1; reaction temperature, 65 °C].

Calcium oxide has also been tried in combination with other compounds to enhance its catalytic activity. Wet impregnation combined with thermal treatment method was used to adhere aqueous solutions of calcium acetate on porous silica (such as SBA-15), MCM-41, and fumed silica, and tried as catalyst for biodiesel development from castor and sunflower oils. CaO was incorporated on porous silica after drying and calcining at 60 °C and 600 °C, respectively. The siliceous support was found to have an important influence on the activity of the catalyst. Among the catalysts, SBA-15 possessed highest thermal stability at a higher calcination temperature of 800 °C and did not suffer any structural modifications. CaO (14 wt.%) supported on SBA-15 was found to be most active for reaction and thermally resistant. High calcination temperature (800 °C) has been reported to transform the calcite phase ($CaCO_3$) and the calcium hydroxide into calcium oxide. An important finding by incorporation of CaO on silica was prevention of lixiviation of the active phase in methanol. CaO and carbonate particles adhered to the surface of the catalyst. The catalyst was found to work differently for different vegetable oils. Yield of 95% was achieved with sunflower oil in 5 h reaction time at a high rate of stirring (1250 rpm) which will consume ample amount of energy. With castor oil as feedstock, yield was comparatively less (65.7%) in 1 h reaction time. This however remains unexplained [20]. Various alkali compounds ($LiNO_3$, $NaNO_3$, and $KNO_3$) were doped on CaO and MgO to foresee their activity in the transesterification reaction. A correlation was observed between the base strength and the activity of the catalyst. Calcination of the catalyst resulted in decrease in the surface area of the catalyst from 10 to 1–2 $m^2/g$. Higher surface area of the catalyst is not even desired as triglycerides are large molecules and would not be able to diffuse into the pores unless a mesoporous substrate is used [21]. Conversion obtained from uncalcined catalysts ($LiNO_3/CaO$, $KNO_3/CaO$, and $NaNO_3/CaO$) was found to be 85%, 90% and 98%, respectively. When the catalysts were calcined, the conversion reached 99–100%. However, when the alkalis were doped with MgO, only 4–5% conversion was achieved. On calcination, only $LiNO_3/MgO$ gave complete (100%) conversion. Even after calcination, $KNO_3/MgO$ and $NaNO_3/MgO$ gave conversion of 4% and 7%, respectively. Leaching of the catalyst was observed when the residual alkali metals in reaction mixture were determined by flame photometry and atomic absorption spectrometry (AAS), resulting in a homogeneous state, which is a major constraint for their application as a heterogeneous catalyst [21]. CaO doped with lithium nitrate ($LiNO_3$) by wet impregnation method has shown increase in its basicity. The base strength ($pK_{BH+}$) of the impregnated catalyst (i.e. Li/CaO) ranged from $15.0 < pK_{BH+} < 17.2$, which is much higher than that of CaO (in the range $8 < pK_{BH+} < 10$). Loading of $LiNO_3$ on CaO resulted in micropore blockage of the catalyst due to crystallization of the $LiNO_3$ phase. This caused decrease in the surface area from 20 to ca. 8 $m^2/g$ for 4 wt.% of Li/CaO catalyst. Loading of lithium in optimum amount (1.23 wt.%) resulted in adsorption of $LiNO_3$ in the form of $Li^+$ and $NO_3^-$ ions on CaO. The formation of electron-deficient $Li^+$ species as confirmed by X-ray photoelectron spectroscopy (XPS) generates defect sites and forms surface hydroxyl (–OH) species in the presence of water. While CaO exhibited 2.5% conversion in 20 min, 100% conversion was achieved from CaO with optimum lithium loading. The lithium leaching from $LiNO_3$-loaded CaO has been reported to be negligible, which is necessary for the catalyst to be classified as heterogeneous [22]. A simple method of activation of CaO as a catalyst has been performed at low temperature. With non-activated CaO, the yield increased substantially after 6 h reaction time. This gave an indication that the CaO was activated by reaction with methanol. To check this, the catalyst was prepared by mixing it with methanol and activated by stirring it for 1 h at 25 °C. Subsequently, rapeseed oil was added and heated at 60 °C for 10 h. Although the reaction rate was found to be low initially (resulting in only 30% biodiesel yield in 1 h reaction time with 0.50 g activated CaO), the yield of the biodiesel was similar to that of well-established homogeneous catalyst, i.e. KOH in 3 h of reaction time. The mechanism proposed for the activated CaO is transformation of a small amount of CaO to $Ca(OCH_3)_2$. Water is generated in the formation of $Ca(OCH_3)_2$ which reacts with the remaining major portion of CaO to form $Ca(OH)_2$. The basic strength of $Ca(OCH_3)_2$ ranged from 11.1 to 15.0, which is higher than non-activated CaO, $Ca(OH)_2$, and activated CaO, which ranged from 10.1 to 11.1. Hence, $Ca(OCH_3)_2$ has a higher catalytic activity. $Ca(OCH_3)_2$ further reacts with glycerol formed as by-product and the CaO-glycerin complex, which also possesses high catalytic activity, advances the reaction. The formation of $Ca(OCH_3)_2$ and CaO–glycerin complex using activated CaO as catalyst is proposed to accelerate the transesterification reaction [23]. CaO has also been used with sunflower oil for biodiesel development under supercritical conditions. Yield of methyl ester increased when CaO was added in supercritical conditions as a catalyst. The reaction took just 6 min. for completion at 252 °C, 41:1 (methanol to oil) molar ratio, and 3 wt.% CaO (Fig. 6). However, this did not seem to be practical because without catalyst, similar conversion has been achieved in 20 min reaction time under supercritical conditions [24].

Leaching aspects of CaO as heterogeneous catalyst have been investigated by Granados et al. [25]. To avoid the influence of air and moisture, in situ studies were carried out. Filtration of the products was done by submerging the basket in reaction medium. Conductivity of the liquid in contact with the catalyst was also determined in situ. It was observed that CaO was more soluble in glycerol–methanol and biodiesel–glycerol–methanol mixtures compared to that in methanol. The larger solubility of CaO in glycerol mixture was attributed to the formation of calcium diglyceroxide, which was formed from reaction of CaO and glycerol. The activity of the leached catalyst was observed to be small in comparison to that arising from the heterogeneous site when the catalyst loading was more than 1 wt.% CaO.

Lanthanum, when added to calcium oxide, has enhanced the basic strength, total basicity, and Brauner, Emmet and Teller (BET) surface area of the catalyst. A high yield (94.3%) was achieved with 20:1 (alcohol to oil) molar ratio, 5% catalyst dose, in 60 min reaction time with refined soybean oil. High yield (96%) was also achieved with crude oil and waste cooking oil having free fatty acid (FFA) and water content in 3 h reaction time. Fourier Transform Infrared (FTIR) study suggested methanol was adsorbed on the catalyst through –OH bonds, resulting in fatty acid methyl ester formation. When water (4%) was added to the reaction mixture, similar yield of 94.8% was achieved in slightly longer duration (i.e. 90 min) in comparison to 60 min without water content (Fig. 7). Presumably, water did not change the total basicity of lanthanum-loaded CaO. Similarly, FFA amounts up to 3.6% were tolerable for the functioning of the catalyst [26]. Eggshell comprising of calcium carbonate as a major constituent was utilized as a potential catalyst by Wei et al. [27]. The catalyst calcined above 800ºC resulted in formation of CaO and was found to the most active with yield in the range of 97–99%. This is attributed to the formation of crystalline CaO as the active phase. A moderate molar ratio of 9:1 (methanol to oil) at 65 °C reaction time, and 3 wt.% catalyst calcined at 1000 °C resulted in high conversion. The catalyst was reused 13 times without deactivation. Activity was reduced after the 13th run and was finally totally deactivated after 17 runs, after which the catalyst was changed from CaO to $Ca(OH)_2$. Dolomite $\{CaMg(CO_3)_2\}$, a natural rock has been used as a heterogeneous catalyst due to its high basicity, low cost, less toxicity and environmental friendliness [28]. Calcination of parent dolomite at 600–700 °C followed by precipitation from the $Ca(NO_3)_2$ solution and again calcination at 800 °C gave high methyl ester content of 99.5% at 15:1 (methanol to oil) molar ratio. The catalyst was reused 3 times with conversion of 95%. In the fourth and fifth run, conversion reduced to 62.2% and 16.5%, respectively. CaO produced from $Ca(OH)_2$ in the crystalline phase has been assumed to be the major active site in the dolomite after its calcination.

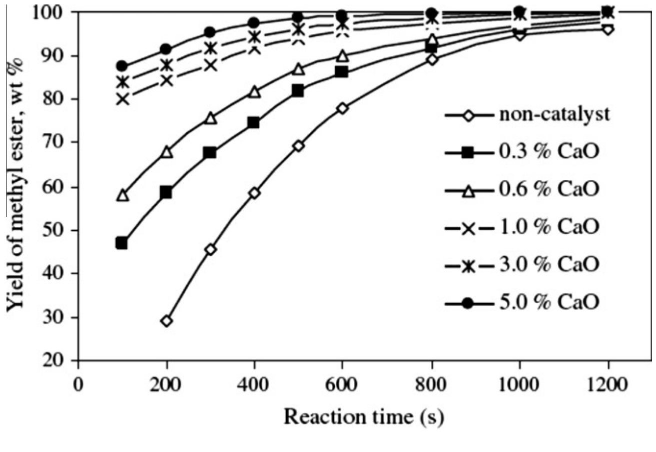

**Fig. 6.** Catalyst, CaO [24]. Effect of CaO content on methyl ester yield. [*Reaction conditions*: methanol to oil molar ratio, 41:1; reaction temperature, 252 °C].

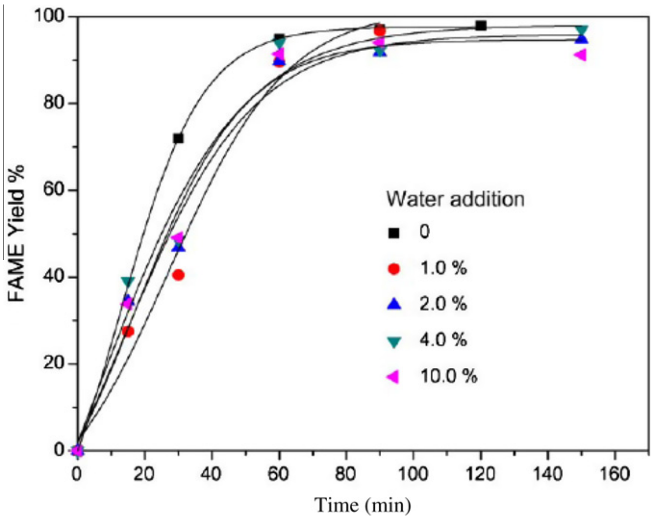

**Fig. 7.** Catalyst, CaO–$La_2O_3$ [26]. Yield of fatty acid methyl ester (biodiesel) with different water addition on $Ca_3La_1$ $\{(La(NO_3)_3$ to $Ca(Ac)_2$ molar ratio 3:1$\}$-catalyzed process. [*Reaction conditions*: $Ca_3La_1$ amount, 5%; methanol to oil molar ratio, 20:1; reaction temperature, 58 °C; reaction time, 90 min].

Economic assessment has also favored CaO as heterogeneous catalyst, which can be separated either by hot water purification process or vacuum distillation process when compared with the similar process adopted with homogeneous catalyst (KOH). It was observed that the manufacturing cost of biodiesel from waste cooking oil using CaO as catalyst manufactured in batch process with a plant capacity of 7260 tonne/year with hot water purification process and vacuum distillation process was 584 and 622 $/tonne of biodiesel. Using KOH as catalyst, the manufacturing cost of biodiesel with same plant capacity utilizing hot water purification process and vacuum distillation process was 598 and 641 $/tonne of biodiesel [29].

### 2.2. Strontium oxide as catalyst

Among alkaline-earth metal oxides, SrO has also attracted attention as a heterogeneous catalyst owing to its high basicity and insolubility in methanol, vegetable oil and methyl esters [30]. A yield of 95% has been attained at a comparatively moderate temperature of approximately 65 °C within 30 min. The catalyst

**Table 1**
Various oxides used as heterogeneous catalysts.

| Heterogeneous catalyst | Calcination | | Reaction conditions | | | Conversion (*C*)/yield (*Y*) (%) | References |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Molar ratio (methanol to oil) | Reaction time (h); temperature (°C) | Catalyst amount (wt.%) | | |
| (SBA-15/MgO) Impregnation method | 450 | 16 | – | 5; 220 | – | *C* = 96.0 | 10 |
| (SBA-15/MgO) In situ coating | 550 | 6 | | | | | |
| KOH/MgO | 500 | 5 | 6:1 | 7–9; reflux of methanol | 3.0 | *C* = 99.4 and *Y* = 95.1 | 11 |
| $K_2CO_3$/MgO | 600 | 3 | 6:1 | 2; 70 | 1.0 | *Y* = 99.0 | 12 |
| Nano MgO | – | – | 36:1 | 0.17; 260 | 3.0 | *C* = 99.3 | 13 |
| $MgO \cdot MgAl_2O_4$ | – | – | – | 10; – | – | *Y* = 57 | 14 |
| CaO | 850–900 | 1.5 | 9:1 | 2.5; 70 | 1.5 | *C* = 93 | 15 |
| Activated CaO | Outgassing at 700 °C | 2 | 13:1 | 1.5; 60 | 1 | *Y* = 94 | 16 |
| CaO | 550 | 5 | 12:1 | 3; 65 | 8 | *Y* = 95 | 19 |
| Calcium oxide supported on mesoporous silica (SBA-15/CaO) | 800 | 1 | 12.1 | 5;60 | 1 | *Y* = 95 | 20 |
| $NaNO_3$/CaO,<br>$KNO_3$/CaO,<br>$LiNO_3$/CaO,<br>$LiNO_3$/MgO | 600 | 5 | 6:1 | 3; 60 | 5 | *C* = 100 | 21 |
| CaO | Activation done by stirring at 25 °C for 1 h | | – | 3; 60 | 2.6 | *Y* = 90 | 23 |
| CaO | Supercritical conditions | | 41:1 | 0.17;252 | 3 | *Y* = 100 | 24 |
| CaO | 430 °C for 1 h, then 750 °C for 8 h, then activation at 750°C for 8 h in pure nitrogen flow | | 20:1 | 1; 58 | 5 | *Y* = 94.3 | 26 |
| CaO from eggshell | 800–1000 | 2 | 9:1 | 3; 65 | 3 | *Y* = 97–99 | 27 |
| CaO from dolomite | i. 600–700 followed by precipitation from $Ca(NO_3)_2$ and then at ii. 800–700 | | 15:1 | 3; 60 | 10 | *C* = 99.9 | 28 |
| SrO | 1200 | 5 | 12:1 | 0.5; 65 | 3 | *Y* > 95 | 30 |

has been reported to have a longer lifetime and could be reused for 10 runs. SrO has been reported to have the advantage of possessing a basic site stronger than $H_- = 26.5$ and is also insoluble in methanol, vegetable oils and fatty acid methyl esters. The reaction mechanism is similar to that of CaO which involves various steps where initially surface methoxide anion ($CH_3O^-$) is formed having high catalytic activity. In the next step, the $CH_3O^-$ attached to the surface of SrO is attracted by the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate. The tetrahedral intermediate formed picks up $H^+$ from the surface of SrO. The final step results in the rearrangement of the tetrahedral intermediates to form biodiesel. Table 1 depicts the oxides used as catalysts and their reaction conditions.

### 2.3. Mixed oxides as catalysts

A mixed oxide of zinc and aluminum has been synthesized for application as a heterogeneous catalyst resulting in high conversion (98.3%) of biodiesel and glycerol of more than 98% purity. A transparent and colorless glycerol is obtained without any ash or inorganic compound. The process of preparation of catalyst has not been described and the study reports utilization of high temperature and pressure during the reaction. This will certainly amount to high cost of biodiesel fuel and will limit its application over other potential catalysts [31]. ZnO loaded to $Sr(NO_3)_2$ and $Ba(NO_3)_2$ has also shown to act as catalyst in transesterification reaction. However, the conversion obtained has been quite low compared to CaO and MgO catalysts discussed above. $Sr(NO_3)_2$ on ZnO was calcined at 600 °C for 5 h. After calcination, 5 wt.% of the catalyst gave conversion of 94.7% with 12:1 (alcohol to oil) molar ratio in 5 h at reflux of methanol. However, when tetrahydrofuran (THF) was used as co-solvent (for better contact of methanol and oil), the conversion increased to 96.8%. The amount of $Sr(NO_3)_2$ loaded on ZnO was optimized to be 2.5 mmol/g. A further increase in this dose resulted in decrease in the activity of the catalyst, which was due to the coverage of the excess $Sr(NO_3)_2$ on surface basic sites. SrO derived from the thermal decomposition of $Sr(NO_3)_2$ after calcination was assumed to possess the main catalytic sites. Thus, conversion is observed to increase only after addition of THF as co-solvent which will incur additional cost and will need additional step for its removal from the product formed as biodiesel [32].

Calcium methoxide, $Ca(OCH_3)_2$, which has often been used as a homogeneous catalyst, has been tried as a heterogeneous solid base catalyst by Liu et al. [33]. By virtue of its low solubility in methanol (<0.04%), high surface area (19 $m^2$/g), and average pore diameter of 40 nm, the catalyst was assumed to be favorable for liquid phase reactions. SEM study revealed large agglomerate particles on the surface of the catalyst. Biodiesel yield of 98% was obtained with 2.0 wt.% of $Ca(OCH_3)_2$ catalyst in 3 h reaction time at 65 °C with a 1:1 methanol to oil volume ratio. The catalyst was reused up to 20 times with yield more than 90%. However, a leachability study was not conducted to ascertain the extent of the heterogeneous nature of the catalyst. $MgO_x(OCH_3)_{2-2x}$ and $Ca(OCH_3)_2$ were tested by Martyanov et al. [34] for their suitability as heterogeneous catalysts for transesterification of tributyrin. Leaching of $Ca(OCH_3)_2$ has been reported where dissolution occurred without deactivation of the catalyst. $Ca(OCH_3)_2$ initially acted as a heterogeneous catalyst, but later its reaction with glycerol (formed as a co-product) resulted in formation of soluble species (i.e. calcium salts of butyric acid) that did not contribute to catalytic activity. $MgO_x(OCH_3)_{2-2x}$, when prepared in the powder form by vacuum evaporation method, possessed weak heterogeneous activity which was attributed to occupancy of the surface of the catalyst by butyric salt species. The catalyst was deactivated after 4 h reaction time,

**Table 2**
Mixed oxides used as heterogeneous catalysts.

| Heterogeneous catalyst | Calcination | | Reaction conditions | | | Conversion (*C*)/yield (Y) (%) | References |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Molar ratio (methanol to oil) | Reaction time (h), temperature (°C) | Catalyst amount (wt.%) | | |
| $Sr(NO_3)_2/ZnO$ | 600 | 5 | 12:1 | 5; 65 | 5 | *C* = 94.7, *C* = 96.8 (with tetrahydrofuron as cosolvent) | 32 |
| $Ca(OCH_3)_2$ | Dried at 105 | 1 | Volume ratio (1:1) | 2; 65 | 2 | *Y* = 98 | 33 |
| $CaMnO_3$,<br>$Ca_2Fe_2O_5$,<br>$CaCeO_3$,<br>$CaZrO_3$,<br>$CaTiO_3$ | For $CaTiO_3$, first at 500 °C, then at 1500 °C for 2 h For $Ca_2Fe_2O_5$ and others, first at 900 °C, then at 1500 °C for 4 h | | 6:1 | 10;60 | 10 | *Y* = 79–92 | 35 |
| CaO·ZnO | 800 | – | 30:1 | 1; 60 | 10 | *C* = 94.2 | 36 |
| Mg–Ca oxide | 500 | 6 | 12:1 | 60 | 2.5 | *Y* = 92 | 38 |

possibly due to the accumulation of the butyric salt species on the surface of the catalyst.

Various metal oxide catalysts such as $CaMnO_3$, $Ca_2Fe_2O_5$, $CaCeO_3$, and $CaZrO_3$ gave methyl ester yield ranging between 79% and 92% at 60 °C 6:1 (methanol to oil) molar ratio in 10 h. A long reaction time and moderate conversion is unlikely to be adopted on a commercial scale of production of biodiesel. The basic strength ($H\_$) of these catalysts were in the range $7.2 < H\_ < 9.3$. $CaTiO_3$, with basic strength of $6.8 < H\_ < 7.2$, gave an average yield of 79% in 10 h. $CaTiO_3$, when reused, gave biodiesel yield of 79% in the first re-run in 10 h reaction time. Surprisingly, in the second re-run, yield increased to 85%. However, catalytic activity decreased in the third re-run and yield reduced to 68% and almost nil (1%) when used for the fourth time. The reason attributed for the decline in catalytic activity is the obstruction of catalytic activity by glycerin and adsorption of fatty acids to the active sites of the catalyst. Another reason for the decreased catalytic activity is thought to be dissolution of catalytic-active species by the glycerin solution. Similar trends were observed with $CaMnO_3$ and $Ca_2Fe_2O_5$. On the other hand, $CaZrO_3$ and $CaCeO_3$ were used for 5 and 7 times, respectively, with a methyl ester yield greater than 80%. $CaCeO_3$ has been reported to be CaO-supported on $CeO_3$ which imparts a better stability and active basic sites to the compound [35]. Leaching studies were not conducted to see if there was any leaching of the catalyst.

Ca–Zn mixed oxides (CaO·ZnO) prepared by co-precipitation have been used as catalysts for transesterification by Ngamcharussrivichai et al. [36]. The mixed oxide contained CaO and ZnO as nano-clusters possessing smaller particle size and high surface area in comparison to pure CaO and ZnO. Increasing the amount of Zn in the mixed oxide resulted in particle size reduction, thus increasing surface area and hence enhancing the activity of the catalyst. The mixed oxide resulted in decreased calcination temperature (785 °C) required for decomposition of calcium carbonate. Complete decomposition of $CaCO_3$ occurred at 800 °C. Adding $Na_2CO_3$ as co-precipitant resulted in formation of CaO·ZnO, which proved to be an even better catalyst. Ca–Zn ratio of 0.25:1 and calcination temperature of 800 °C gave methyl ester yield of 94.2%. A Ca–Zn ratio > 1 decreased the yield substantially. Reaction conditions were: a high molar ratio, i.e. 30:1 (methanol to oil); catalyst 10 wt.%; in 3 h at 60 °C. A comparatively high molar ration and high quantity of catalyst will incur high cost too. However, the study is significant in reducing the calcination temperature of $CaCO_3$ and Reuse of the catalyst gave yield of more than 90% up to 3 times after washing with methanol and 5 M ammonium hydroxide [36].

A study on continuous process for development of biodiesel by porous zirconia, titania and alumina micro particulate for simultaneous esterification and transesterification of fatty acids has been described by McNeff et al. [37]. This Mcgyan process (named after the three inventors: McNeff, Gyberg, and Yan) uses supercritical methanol as reactant and does not require surface modification of the catalyst. The process is anticipated to reduce the production cost of biodiesel as feedstock with higher FFA could be converted to fatty acid alkyl esters. Titania catalyst was reused effectively up to 115 h of continuous operation without loss of activity. The process has been quite effective for algae as potential and suitable feedstock because algae possesses higher fatty acids and can grow rapidly under controlled conditions [37]. Mixed Mg–Al and Mg–Ca oxides were compared as catalyst for transesterification reaction. Mg–Ca oxide performed better owing to high surface area and presence of strong basic sites on the surface coming from $Ca^{2+}$–$O^{2-}$ pairs. Ninety two percent yield was achieved by the catalyst with optimized reaction conditions of 12:1 alcohol to oil molar ratio at 60 °C reaction temperature [38]. Mg–Al mixed oxide as catalyst in the reaction medium caused leaching leading to both homogeneous and heterogeneous pathway. Yield of 93% was obtained under optimized reaction conditions. The basicity of the Mg–Al mixed oxide contributed only 23% yield of methyl ester and the rest of the yield was attributed to the leached catalyst which indicates the catalyst to be more of homogeneous nature and hence unsuitable for use as solid catalyst [39]. Table 2 lists the mixed oxides used as catalysts along with the reaction conditions.

## 3. Hydrotalcite/Layered Double Hydroxide (LDH) derived catalysts

Hydrotalcite or Layered Double Hydroxide (LDH) is an anionic and basic clay found in nature with the general formula of $([M^{z+}_{(1-x)}M^{3+}(OH)2]^{b+}(A^{n-}_{b}/n)\cdot M\ H_2O)$, where $M^{z\ +}$ is a divalent or monovalent cation and $A^{n-}$ is the interlayer anion [40]. A pioneering work on hydrotalcites being used as catalyst for synthesis of biodiesel has been provided by Helwani et al. [1] and Zabeti et al. [3]. Hydrotalcites/LDH has been used as catalyst as well as support for exogenous catalytic species. Catalyst supported on LDH, may be at the surface or between the LDH structure layers. The value of $x$ usually ranges from 0.20 to 0.33. However, reports are also available with value of $x$ higher than 0.33. Hydrotalcite are an important group of catalyst as their acid and basic properties can be controlled by varying their composition and hence have been tried extensively for synthesis of biodiesel. The commonest hydrotalcite is $Mg_6Al_2(OH)16CO_3{\cdot}4H_2O$ and the conventional method of its synthesis is co-precipitation method [1]. Siano et al. [41] observed that the Mg/Al molar ratio of 3–8 was optimum for high catalytic activity was found to be active even in the presence of high amount of water (i.e. 10,000 ppm). Di Serio et al. [6] reports four groups of basic sites to be found in Mg–Al hydrotalcites. These includes weak basic site related to $OH^-$ surface groups; medium basic site related to oxygen in MgO and $Al_2O_3$; and strong basic sites and super-basic sites related to $O^{2-}$ anions. Mg–Al hydrotalcites also possesses large pore size which result in its high catalytic activity in comparison to that of MgO. Mg–Al hydrotalcites ($[Mg_{2+1-x})Al_x(OH)_2]_x + (CO_3)^{2-}_{x/n}$) synthesized via alkali-free co-precipitation method were effective for biodiesel synthesis. $(NH_4)_2CO_3$ and $NH_4OH$ were used as precipitation agents for catalyst preparation [42]. High pH facilitated the incorporation of Mg into the hydrotalcite owing to increased solubility of $Mg(OH)_2$ over $Al(OH)_3$. Hydrotalcites possessed larger pores (20 nm) than $Al_2O_3$ and MgO. The activity of higher-loaded Mg hydrotalcites (21–24 wt.%) was found to be comparable to that obtained by Li-doped CaO solid base catalyst reported by Watkins et al. [22]. The increase in basicity of the catalyst has been attributed to increased intralayer electron density of Mg-rich hydrotalcites.

Calcined Mg–Al hydrotalcite {$Mg_6Al_2(OH_{16})CO_3 \cdot 4H_2O$, which had earlier been used as a heterogeneous catalyst in various base-catalyzed reactions (Aldol condensations, Michael reaction, cyanoethylation of alcohols, and nitroaldol reaction) has been used for transesterification reaction by Xie et al. [43]. $Mg_6Al_2(OH_{16})$-$CO_3 \cdot 4H_2O$ has been used for transesterification reaction of soybean oil. Part of the $Mg^{2+}$ in the hydrotalcite is assumed to be replaced by $Al^{3+}$ ions, forming positively charged layers. Calcination at higher temperature decomposes the hydrotalcite into interactive and well-dispersed Mg–Al oxides of higher surface area possessing hydroxyl groups and strong Lewis basic sites associated with $O^{2-}M^{n+}$ acid–base pairs. Basic sites associated with structural hydroxyl groups and strong Lewis basic sites associated with $O^{2-}M^{n+}$ acid–base pairs are developed. Conversion of the soybean oil to methyl esters increased with hydroxyl value of the liquid phase. Maximum basicity was observed at an Mg/Al molar ratio of 3.0, beyond which the basicity of the catalyst decreased (Fig. 8). The basic strength of the samples ranged from 9.3 to 15.0. The main basic sites were observed in the $H\_$ range of 7.2–9.8. Other sites were also observed in the H_ range of 9.8–15.0. Conversion obtained was 67% with 600 rpm and 35% with 100 rpm. Although only 67% conversion of the feedstock to esters was achieved, Xie et al. [43] found the catalyst was easily separable. Though still, this will not justify its application as heterogeneous catalyst as the European Norm (EN) states conversion to be at least 96.5%. In Mg–Al hydrotalcite-derived catalyst {$Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$} for the transesterification of poultry fats, basic site was found to be the influencing factor for the transesterification reaction. Influence of Lewis acid sites (from $Al^{3+}$ centers) was observed to have limited role in the reaction. The calcination temperature has also been reported to be one of the important factors for the performance of heterogeneous catalysts. Sufficient temperature during the calcination process should be induced so as to break down the ordered structure, remove the counter-balancing anions, and induce phase transitions within the oxide lattice. However, calcination temperature should not be so high as to avoid the formation of $MgAl_2O_4$ and the segregation of the alumina phase. The catalyst was deactivated after the first reaction cycle which is attributed to deactivation of the strongest accessible base sites. However, simple re-calcination in air allowed the complete restoration of the catalyst. Maximum yield (94%) and conversion (98%) of fatty acid methyl ester was observed at a high molar ratio (60:1) of methanol to oil in 6 h reaction time, but the separation of biodiesel and glycerol was not sharp. At a lower molar ratio, the time taken to attain similar conversion was 3, 5, and 15 times more with molar ratio 30, 15, and 6 respectively. Such a high molar ratio will add to the cost of biodiesel and will not be favored at industrial level of production. Addition of a co-solvent such as tetrahydrofuran, hexane, or toluene could not enhance the conversion of poultry fats. However, Mg–Al mixed oxide was found to be thermally and mechanically stable and no significant difference was observed in particle size and morphology of the used catalyst as evidenced by SEM. The similar Mg–Al ratio of the fresh and used catalyst also confirmed that the catalyst did not leached in the reaction mixture [44]. Hydrotalcite prepared by co-precipitation method has also been used for immobilization of lipase and was found to effectively produce methyl esters from waste cooking oils with yield of 92.8% as compared to 95% obtained from free enzyme solution. However, the time required to attain optimum yield was 105 h which is lengthy in comparison to that taken by other solid catalysts and will pose a constraint at industrial level of production (Fig. 9) [45].

Hernandez et al. [46] have done a modification by loading sodium in calcined hydrotalcite to enhance the activity of the catalyst. The catalyst was found to work at a low temperature (60 °C) and with neat soybean oil and used frying oil with an acid value of 0.08 and 1.9 mg KOH/g respectively. The Mg–Al mixed oxide was calcined at 500 °C for 8 h and sodium was incorporated using sodium acetate. The yield of methyl ester obtained was 88% and 67% for soybean oil and used frying oil respectively [46]. A hydrotalcite, $[Zn_{1-x}Al_x(OH)_2]^{x+}\,(CO_3)_{x/2n} \cdot mH_2O$ has been used as a precursor to prepare Zn/Al complex oxide catalyst tolerant to FFA and water content in oil. The oil conversion was more than 83.6% with

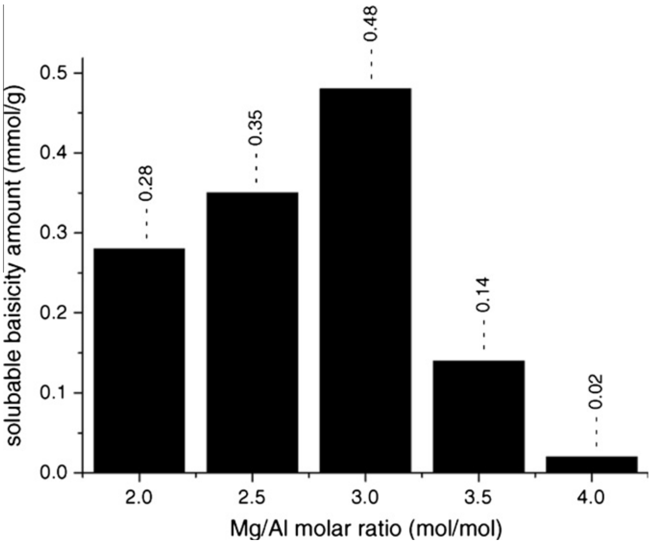

**Fig. 8.** Catalyst, calcined Mg–Al hydrotalcite [43]. Soluble basicity of hydrotalcite with different Mg/Al molar ratios. [*Reaction conditions*: methanol to oil molar ratio, 15:1; catalyst amount, 7.5%; reaction time, 9 h; reaction temperature, methanol reflux].

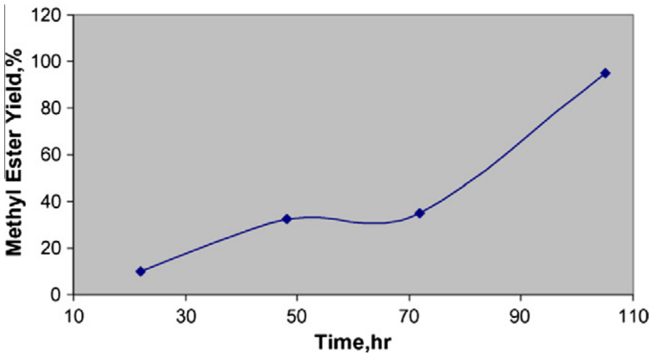

**Fig. 9.** Catalyst, hydrotalcite immobilized by lipase [45]. Effect of reaction time on methyl ester yield. [*Reaction conditions*: reaction time, 22–105 h; reaction temperature, 24 °C].

water content as high as 10% and FFA content up to 8 wt.% under optimized sub critical reaction conditions. The catalyst got deactivated possibly by adsorption of oil on the surface of the catalyst and was regenerated by immersing in an alkali solution and incinerating it at 400 °C [47].

The immobilization of enzyme on Mg–Al hydrotalcite was found to modify the microenvironment of lipase and minimize the affect of external factors such as temperature, pH, and ionic species thus being more stable than free lipase. The immobilized lipase (*Saccharomyces cerevisiae*) from yeast was found to retain 95% catalytic activity in comparison to 88% by free lipase [48]. Conversion of 96% was achieved in considerable reaction time (4.5 h). Conversion increased to 96.4% with the addition of a small amount of water (i.e. 2.0 wt.%) which enhanced the esterification rate. More water caused hydrolysis and hence decreased conversion. However, the immobilized lipase was sensitive to FFA, and optimum conversion was obtained at acid value 0.5 mg KOH/g. The conversion of methyl esters decreased with increase in acid value. Conversion of methyl esters gradually dipped to 81.7% at 3.5 mg KOH/g acid value. With increase in acid value (4 mg KOH/g), conversion was 66.9% which further decreased to <50% when the acid value of feedstock was 6 mg KOH/g. Conversion >81% was observed till 10 runs and gradually decreased after subsequent runs. At the end of the 14th run, 54.1% conversion was achieved. This has been attributed to the formation of water as co-product, enzyme denaturation, and loss of enzyme during filtration.

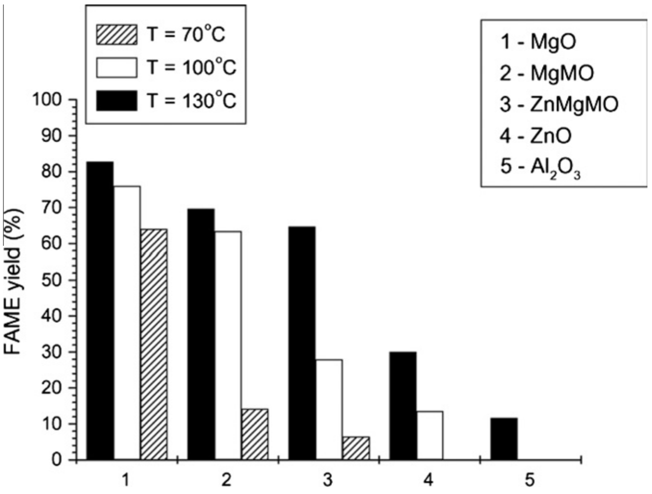

**Fig. 10.** Catalyst, MgO, MgMO, ZnMgMO, ZnO, $Al_2O_3$ [51]. Methyl esters yield for the catalysts at different temperature. [*Reaction conditions*: methanol to oil molar ratio, 55:1; reaction time, 7 h].

Contrary to this Barakos et al. [49] report that FFA enhanced the conversion by acting as acid homogeneous catalyst simultaneously with Mg–Al–$CO_3$ hydrotalcite catalyst. The activity of the calcined catalyst was found to be lower than the initial activity of the non-calcined catalyst. Final yield achieved was the same with uncalcined, calcined catalyst, and reused catalyst. However, the non-calcined catalyst was deactivated after transesterification reaction, which has been attributed to high temperature (200 °C) adopted during the reaction. Ninety nine percent conversion was achieved with cotton seed oil having higher acid value and water content in 3 h reaction time. The catalyst could perform esterification as well as transesterification reaction [49].

Mg–Al hydrotalcites after calcination at 500 °C for 12 h gave 90.5% conversion of biodiesel. The conversion is low as per the EN norm. However, the reaction conditions used were moderate, i.e. 6:1 (alcohol to oil) molar ratio, 1.5 wt.% catalyst, and 4 h reaction time at 65 °C and moderate rate of stirring (300 rpm). The catalyst was found to be separable by filtration and was recycled for 3 runs with a minor loss in its activity (>88% conversion) [50]. 1.5% potassium loaded on Mg-Al hydrotalcite was found to enhance the catalytic activity of hydrotalcite and gave a high conversion (96.9%) and yield (86.6%). However, longer duration for calcination (35 h) was required for synthesis of the catalyst which is energy intensive. Biodiesel developed was blended with diesel {to form B10, i.e. 90 part diesel and 10 part biodiesel (v/v)} and its impact on performance of elastomers in the fuel system component were close to that of diesel and established its compatibility [51].

KF loaded on hydrotalcite by co-precipitation method was found to have enhanced activity as catalyst. After loading with KF, a new phase formation of $KMgF_3$ and $KAlF_4$ was observed and assumed to be the active component of the catalyst. An 80% (wt/wt) load ratio of KF/hydrotalcite with 12:1 (alcohol to oil) molar ratio gave a yield of 92% in 5 h reaction time at 65 °C [52].

**Table 3**
Hydrotalcite/layered double hydroxide based heterogeneous catalysts.

| Heterogeneous catalyst | Calcination | | Reaction conditions | | | Conversion (*C*), yield (*Y*) (%) | References |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Molar ratio (methanol to oil) | Reaction time (h), temperature (°C) | Catalyst amount (wt.%) | | |
| Mg–Al hydrotalcite $Mg_6Al_2(OH_{16})CO_3 \cdot 4H_2O$ | 500 | 8 | 15:1 | 9; reflux of methanol | 7.5 | *C* = 67 | 43 |
| Na/hydrotalcite with soybean oil | 500 | 8 | 15:1 | 8; 60 | 7.0 | *Y* = 88 | 46 |
| Na/hydrotalcite with used frying oil | | | 9:1 | 8; 60 | 7.0 | *Y* = 67 | |
| Zn/Al complex oxide derived from hydrotalcite | 450 | 8 | 24:1 | 1.5; 200; Pressure = 2.5 MPa | 1.4 | *C* = 83.6 | 47 |
| Mg–Al–$CO_3$ hydrotalcite | 350 | 6 | 6:1 | 3; 180–200 | 1 | *C* = 99 | 49 |
| Mg–Al hydrotalcites | 500 | 12 | 6:1 | 4; 65 | 1.5 | *C* = 90.5 | 50 |
| Mg–Al hydrotalcite | 450<br>500 (after loading with potassium acetate) | 35<br>2 | 30:1 | 6; 100 | 7 | *C* = 96.9, *Y* = 86.6 | 51 |
| KF/hydrotalcite | 450 | 3 | 12:1 | 5; 65 | 3.0 | *Y* = 92 | 52 |
| KF/Ca–Al hydrotalcite | 550 | 5 | 12:1 | 3; 65 | 5.0 | *Y* = 99.74 | 53 |
| $(Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O)$ | – | – | 6:1 | (Time not reported); 140 | 6.0 | *C* = 95.7 | 56 |
| Mg–Co–Al–La Layered double hydroxide | 600 | 4 | 16:1 | 5; 200 | 2.0 | *Y* = 96–97 | 57 |
| $[Al_2Li(OH)_6](CO_3)_{0.5} \cdot nH_2O$ | 500 | 2 | 15:1 | 1; 65 | 1 | *Y* = 83.1 | 58 |

The catalytic activity was further enhanced by loading KF on Ca–Al hydrotalcite prepared by co-precipitation method and a high yield of 99.74% was obtained. The new crystal phases $KCaF_3$, $KCaCO_3F$, and $CaAl_2F_4(OH)$ were believed to be the active component in the modified catalyst [53]. Mixed oxides {Mg(Al)O and ZnMg(Al)O} were tried as solid base catalysts but their activity were found to be lower than that obtained from MgO and a high temperature (100–130 °C) was required. Among Mg(Al)O and ZnMg(Al)O, comparatively high yield was achieved with former than latter. With ZnO and $Al_2O_3$, the yield obtained was less than 40% (Fig. 10) [54].

Poly(vinyl) alcohol membrane was been loaded with hydrotalcite and found to enhance the activity of the catalyst [55]. The membrane embedded with poly(vinyl) alcohol matrix was made hydrophobic either by total or partial acetylation (by treating with acetic anhydride) or by treatment with succinic anhydride. The modified catalyst was found to exhibit activity for more than 20 times as compared to the unsupported catalyst. After seven runs the modified catalyst exhibited catalytic activity three times more than the unsupported fresh hydrotalcite. The good activity of the catalyst has been attributed to comparatively better swelling for both the soybean oil and methanol.

Zinc hydroxide nitrate, $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$, a layered hydroxide salt, was found to be effective for esterification as well as transesterification reaction. However, the reaction condition reported was energy intensive (140 °C) during esterification and transesterification {150 °C at 48:1 (methanol to oil) molar ratio} [56]. The $Mg_3Al$-LDH catalyst was found to give good catalytic activity but got gelled which inhibited the possibility of its reuse. This was overcome by incorporation of Co and La to the mixed oxide to form spinal phase. The catalyst developed as Mg–Co–Al–La resulted in high yield (96–97%) at 200 °C, 16:1 (ethanol to oil) molar ratio and was reused for at least 7 times [57]. Li–Al LDH, i.e. $[Al_2Li(OH)_6](CO_3)_{0.5}{\cdot}nH_2O$ was found to give better activity after calcination in comparison to Mg–Al, and Mg–Fe type LDH. To test the heterogeneous nature of the catalyst, it was stirred in methanol for 1 h and then filtered. The filtrate showed a trace amount of lithium imparted by the catalyst. Although minimal amount of leaching of lithium was observed during batch transesterification reactions, the authors' reports to be further working on fixed bed mode of experiments for a comprehensive study on leaching and stability aspect of the catalyst [58]. Various hydrotalcite/LDH catalysts and their reaction conditions for synthesis of biodiesel are summarized in Table 3.

## 4. Solid superbase catalyst

A rare earth metal oxide ($Eu_2O_3$) has been tried as heterogeneous catalyst by Sun et al. [59]. KF loaded on $Eu_2O_3$ prepared by impregnation method and calcined at 600 °C for 4 h resulted in formation of $F^-$, thus introducing KOH or hydroxyl groups on the surface of the catalyst and enhancing its activity. $H\_$ of the catalyst was above 15.0, showing it to possess strong basic sites at its surface. $Eu_2O_3$ loaded with 15 wt.% KF gave sufficiently high yield (92.5%) under optimized reaction conditions. For the reuse application of the catalyst, it was found that 15 wt.% KF has to be added to the catalyst which got deactivated to achieve high yield (87.3%). However, the leaching aspect of the catalyst was not determined to check its residual amount in the products.

## 5. Alumina loaded with various compounds as catalyst

Aluminum is the third most abundant element in the earth's crust and its oxides have been utilized extensively as a potential heterogeneous catalyst. Although alumina is acidic in nature, its potential as a heterogeneous catalyst after loading with a base compound has been an area of interest. Alumina loaded with various compounds has been found to be an efficient catalyst for synthesis of biodiesel. Lacome et al. [60] report that 12.5 wt.% of $TiO_2$ supported on $Al_2O_3$ was found to give 95% yield. However, a high amount of methanol (as evident from 1:1 mass ratio of methanol to oil), high temperature (200 °C) and high reaction time (7 h) were needed for the reaction. Na/NaOH/$\gamma$-$Al_2O_3$ used as a heterogeneous catalyst along with the co-solvent *n*-hexane has shown activity similar to that of the homogeneous one (i.e. NaOH with a yield of 94% in 2 h reaction time at 60 °C and 9:1 alcohol to oil molar ratio) with moderate rate of stirring (300 rpm). The catalyst was prepared by treatment of $\gamma$-$Al_2O_3$ with sodium hydroxide followed by sodium at 320 °C under controlled nitrogen flow. Loaded sodium has been proposed to be completely ionized and dispersed into the defect sites of $\gamma$-$Al_2O_3$ which was formed during thermal pretreatment [61]. The electron pair donating ability of surface oxygen atoms present on the catalyst was enhanced and developed strong basic sites on the catalyst. 20 wt.% Na and 20 wt.% NaOH incorporated on $\gamma$-$Al_2O_3$ showed the highest activity. However, leaching studies of the catalyst have yet to be performed to ascertain the extent of heterogeneity of the catalyst [61]. An alkali metal salt, $K_2CO_3$ loaded with alumina ($Al_2O_3$) by impregnation method, was investigated for transesterification of triolein and resulted in 94% and 89% yield of ester and glycerol, respectively, at 60 °C in 1 h reaction time. This is significant as moderate temperature conditions and less time are employed for a good yield (94%) of biodiesel. It was observed that basic strength did not necessarily enhance a better conversion. The catalytic activity of $K_2CO_3/Al_2O_3$ was found to be comparable to that obtained from 0.023 mmol of KOH. Presence of water (0.5 mmol) while using $K_2CO_3/Al_2O_3$ as catalyst slightly increased the yield of methyl oleate giving an indication that reaction is not sensitive to presence of water [62]. A solid base catalyst of $KNO_3$ loaded on $Al_2O_3$ resulted in formation of $K_2O$ phase causing high catalytic activity. $KNO_3$ (35 wt.%) calcined at 500°C for 5 h provided a high basic strength in the range 15–18.4 (corresponding to 6.67 mmol/g). $K_2O$ along with surface Al–O–K were considered to be the main active sites that resulted in moderate conversion (87.4%) of the soybean oil to methyl esters. It was found that optimum conditions for reaction were 15:1 M ratio with a catalyst amount of 6.5% in 7 h. [63]. $Al_2O_3$ loaded with 35 wt.% $KNO_3$ by impregnation method has also been tried by Vyas et al. [64]. A moderate conversion (84%) has been achieved after calcining the catalyst for 4 h at 500 °C and undergoing transesterification reaction with a methanol to oil molar ratio of 12:1 and 6% catalyst for 6 h reaction time at 70 °C and 600 rpm agitation. Kinetic studies of the experiments were carried out and activation energy (*E*) was determined to be 26.96 kcal, which was low enough to make the reaction insensitive to temperature. Attempts to reuse the catalyst after drying and calcination gave reduced conversion of methyl esters of 75% and 72% in the 2nd and 3rd runs, respectively [64]. The catalyst owing to its moderate conversion efficiency may not find application at industrial level of production.

Xie et al. [65] report base strength and the amount of base sites to be important parameters for the activity of heterogeneous catalyst. The potential of alumina ($Al_2O_3$) loaded with various potassium compounds have shown varying catalytic activity. While, conversion was not obtained with $Al_2O_3$, and $Al_2O_3$ loaded with KCl; 87.4%, 85.8%, and 80.2% conversion were obtained with $Al_2O_3$ loaded with KI, KF, and KOH respectively. The basic strengths of these compounds with successful conversion were in the range 15.0–18.4 and assumed to be an important factor in catalyst activity. Other potassium compounds (KBr and $K_2CO_3$) loaded with $Al_2O_3$ showed conversion of less than 50%. These compounds showed $H\_$ in the range 9.3–15.0. $Al_2O_3$ and $KCl/Al_2O_3$ showed no reaction and had the weakest $H\_$ of less than 7.2. KI, which showed best catalytic activity, was then loaded on different carriers such as

$ZrO_2$, ZnO, and NaX. KI/$Al_2O_3$ displayed best catalytic activity with 87.4% conversion, followed by $ZrO_2$ and ZnO showing 78.2% and 72.6% conversion, respectively. Other carriers (NaX and KL) showed conversion of less than 30%. On increasing the catalyst amount a high conversion of 96% with 2.5 wt.% of catalyst was observed with KI/$Al_2O_3$.

NaOH, a homogeneous catalyst have been loaded on $\gamma$-$Al_2O_3$ and its activity have been compared by Arzamendi et al. [66]. NaOH-loaded $\gamma$-$Al_2O_3$ catalyst dried at 120 °C for 12 h was active enough for transesterification reaction. For homogeneous catalysis with NaOH, the ratio of catalyst to methanol was an important factor for the initial rate of transesterification reaction. Contrary to this, the heterogeneous catalyst NaOH/$\gamma$-$Al_2O_3$ was dependent on the methanol to oil molar ratio applied for the reaction. Eighty two percent conversion was achieved at 6:1 (methanol to oil) molar ratio and increased to 88% at 12:1 M ratio. The reaction almost completed when the alcohol to oil molar ratio was raised to 24:1 because this high ratio favored the formation of methoxide, which enhances the reaction rate. The extent of leaching was within 5% after 9 h reaction time. Nevertheless, the low amount of leached catalyst will have to be removed to make the biodiesel product usable and acceptable in the market [66]. A three step calcination at 300 °C, 550 °C, and 900 °C for 2, 3 and 8 h, respectively, transformed $Eu(NO_3)_3/Al_2O_3$ (prepared by impregnation method) to $Eu_2O_3/Al_2O_3$ and tried as a heterogeneous catalyst for synthesis of biodiesel by Li et al. [67]. The catalyst, $Eu_2O_3/Al_2O_3$ (6.75% Eu), increased $H\_$ of the catalyst to 26.5 and augmented superbase sites on its surface. A moderate conversion (63.2%) has been reported from the catalyst at a temperature of 70 °C in 8 h reaction time with 10 wt.% catalyst. Conversion is far below the minimum regulatory specification by EN norms and seems not suitable for application as heterogeneous catalyst. Repeated use of the catalyst further resulted in decrease in the conversion of fatty acids to 35.3% after 40 h reaction time. This has been attributed to loss of the catalyst during its filtration and re-calcination, which amounted to 6%. Reduction in BET surface area was also observed for the used catalyst in subsequent runs which amounted to its deactivation [67]. The leaching of potassium on potassium impregnated $\gamma$-$Al_2O_3$ ($K_2CO_3/\gamma$-$Al_2O_3$) catalyst has been studied extensively by Alonso et al. [68]. The catalyst gave 99% yield in 1 h, but when was reused, the catalyst performance was reduced to 33, 6.5, and 3.8% in the 2nd, 3rd, and 4th runs, respectively. Although the catalysts in their reuse application were not activated, such a drastic reduction in yield of biodiesel product was attributed to deactivation of the active sites owing either to catalytic poisoning or the possibility of catalyst leaching. However, even re-calcination of the used catalyst showed low yield (<33%). On the assumption that sintering did not occur on the surface, either $KAlO_2$-like or K–O–Al species is considered to have formed at the surface, the leaching is proposed in the following manner:

$$KAlO_2 + CH_3OH \rightarrow AlOOH + K^+ + CH_3O^- \qquad (1)$$

Solid $KAlO_2$ is probably formed at the surface of the solid catalyst which, on reaction with methanol, produces methoxide ion ($CH_3O^-$), which is responsible for the homogeneous reaction [68]. KF supported on $Al_2O_3$ by impregnation method showed formation of a new phase ($K_3AlF_6$) after calcination. A yield of >90% was obtained under optimal experimental conditions of 12:1 (alcohol to oil) molar ratio at 65 °C in 3 h. However, the catalyst had to be regenerated each time before use. The process of regeneration has not been described and thus needs further study for its approval as a potential heterogeneous catalyst [69]. The test of leaching of heterogeneous catalysts derived from alkaline and alkaline-earth metal oxides during the reaction thus becomes an important aspect to be checked. The type of support is a significant factor for a catalyst to follow the heterogeneous pathway. KOH loaded on $Al_2O_3$ and NaY prepared by impregnation method were studied for transesterification by Noiroj et al. [70]. 25 and 10 wt.% of KOH and NaY loaded on $Al_2O_3$ was found to be optimum. Loading of KOH resulted in the formation of $K_2O$ as an active phase. Increased loading of KOH (i.e. beyond the optimum amount) resulted in formation of another new phase Al–O–K which possessed catalytic activity and basicity lower than $K_2O$. Hence, optimum amount of KOH loading is desirable for better performance of the catalyst. Although yield (91.1%) from both of the catalysts was the same, 51.3% of potassium was leached from KOH/$Al_2O_3$ in comparison to only 3.2% by KOH/NaY. Hence, NaY is assumed to be a good support for $Al_2O_3$ as a heterogeneous catalyst [70].

$Al_2O_3$-supported alkali metal and earth metal oxides were used as catalysts after calcination. High conversions of 94.3% and 91.6% were observed with $Ca(NO_3)_2/Al_2O_3$ and $Li(NO_3)/Al_2O_3$, respectively. $NaNO_3/Al_2O_3$ and $KNO_3/Al_2O_3$ gave low yields of 24.7% and 34.5%, respectively. Calcination of $NaNO_3/Al_2O_3$ and $KNO_3/Al_2O_3$ catalysts could not convert the nitrate precursors to active oxide forms, which was the case when $Ca(NO_3)_2/Al_2O_3$ and $Li(NO_3)/Al_2O_3$ were used as catalysts. Dissolution of $NaNO_3/Al_2O_3$ and $KNO_3/Al_2O_3$ occurred wherein $Na_2O$ and $K_2O$ of about 70 and 45 wt.%, respectively, were observed during the elemental analysis after transesterification. Using $NaAlO_2$ as a commercial catalyst gave 92% methyl ester content under the same reaction conditions and it was assumed that $NaNO_3/Al_2O_3$ and $KNO_3/Al_2O_3$ calcined at higher temperature could have followed the homogeneous pathway. $Ca(NO_3)_2/Al_2O_3$ proved to be best among these catalysts owing to its lowest leachability (only 8 wt.% loss of CaO) [71]. Recently, Umdu et al. [72] used a microalga, *Nannochloropsis oculata*, as feedstock found that alumina loaded on CaO and MgO compounds by modified single step sol–gel method as heterogeneous catalyst was more active than pure CaO and MgO. 97.5% biodiesel yield was achieved with 80 wt.% loading of CaO on $Al_2O_3$. To obtain the high yield from the mixed oxide ($CaO/Al_2O_3$ and $MgO/Al_2O_3$), basic strength was found to play an important role in addition to that by basic site density. Various alumina-based catalysts are shown in Table 4.

**Table 4**
Alumina based heterogeneous catalysts.

| Heterogeneous catalyst | Calcination | | Reaction conditions | | | Conversion (*C*), yield (*Y*) (%) | References |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Molar ratio (methanol to oil) | Reaction time (h); temperature (°C) | Catalyst amount (wt.%) | | |
| $KNO_3/Al_2O_3$ | 500 | 5 | 15:1 | 7; methanol reflux | 6.5 | *C* = 87.4 | 63 |
| $KNO_3/Al_2O_3$ | 500 | 4 | 12:1 | 6; 70 | 6 | *C* = 84 | 64 |
| $KI/Al_2O_3$ | 500 | 3 | 15:1 | 8; methanol reflux | 2.5 | *C* = 96.0 | 65 |
| $Eu_2O_3/Al_2O_3$ | 300 °C for 2 h, 550 °C for 3 h, and 900 °C for 8 h | | 5:1–6:1 | 8, 70 | 10 | *C* = 63.2 | 67 |
| $KF/Al_2O_3$ | 600 | 3 | 12:1 | 3; 65 | 4.0 | *Y* = 90 | 69 |
| $KOH/Al_2O_3$ | 500 | 3 | 15:1 | 2; 60 | 3 | *Y* = 91.1 | 70 |
| KOH/NaY | | | | 3; 60 | 6 | | |

## 6. Zeolites as catalyst

Zeolites are microporous aluminosilicate minerals. They are commonly used as adsorbents for water and wastewater purification. They have also been used as catalyst for fluid catalytic cracking and hydro-cracking in petrochemical industry. Zeolites as catalyst have the characteristics of acidic sites and shape selectivity. Zeolites vary in pore structure and inner electric fields from crystal and surface properties which result in their varying catalytic properties [73]. Zeolites have recently been tried as potential heterogeneous catalyst for synthesis of biodiesel. A variety of zeolites and metals have been tried as catalysts for transesterification of soybean oil possessing free fatty acid (2.6%) by Suppes et al. [74]. The catalysts, ETS-10 ($Na_{21.9}K_{7.5}Ti_{16.5}Si_{77.5}O_{208}$) and $NaO_x$/NaX* (* indicates sodium azide-loaded samples), showed higher conversion of methyl esters (94.6% and 94.2%, respectively) at 120 °C for 24 h owing to their higher basicity and larger pore volume resulting in improved intra-particle diffusion. Optimum conditions were calcination of catalysts at 500 °C, which resulted in the removal of water and carbon dioxide from its surface. At low temperature (60 °C) conversion obtained was less (<85%) even after 24 h reaction time. At 100 °C reaction temperature, 92% conversion was achieved in 3 h with diglyceride and monoglyceride concentration of 4% and 2%, respectively. Presence of FFA had a significant effect on the reaction and reduced the methyl ester conversion to less than 13.7% even after 4 h reaction time. The catalyst has been reused without loss in its activity. As the temperature and time needed for the reaction is high, a cost analysis of the process seems to be a deterrent in their commercialization [74]. NaX zeolites (Si/Al = 1.23) after loading with KOH increased the basic strength from <9.3 to 15.0–18.4. The conversion achieved was moderate (85.6%) by 10% loading of KOH on NaX beyond which its activity decreased owing to agglomeration of active KOH phase and/or the coverage of active base sites. The catalyst was reused after washing with cyclohexane and heating for 2 h at 125 °C. The conversion of the methyl esters then decreased to 48.7%, which was attributed to leaching of KOH. However, when the catalyst was regenerated by impregnation method, the yield obtained was 84.3%, which is comparable to the initial yield achieved. The low conversion obtained with the catalyst indicated presence of tri-, di-, and monoglycerides which makes the biodiesel fuel off specification [75]. Still, the leached catalyst in the mixture cannot be ignored because it will hinder its application as a heterogeneous catalyst. Zeolites (mordenite, beta, and X), when used as heterogeneous catalysts for transesterification of sunflower oil, gave methyl ester contents of 93.5–95.1 wt.% at 60 °C reaction temperature. When the leaching studies were carried out, sodium was found to have leached in the mixture, giving the reaction a homogeneous pathway. However, metal incorporation on the catalyst was observed to be far superior with the widely used impregnation method than with the ion-exchange method. This is attributed to absence of strong basic sites on the catalyst by the ion-exchange technique. However, the method employed for the preparation of the catalyst was longer. This required heating, drying, and calcining at 500 °C for 10 h, 120 °C for 12 h, and 550 °C for 15 h respectively [76]. Y-type zeolites with different $Al_2O_3$ content have yielded a low biodiesel conversions (26.6%) at a high reaction temperature (>450 °C) with a 6:1 alcohol to oil molar ratio for used vegetable oil and seems unsuitable as a heterogeneous catalyst [77]. Zeolites have also been tried as catalysts for conversion of high FFA oils to FAME. NaY zeolites (basic in nature) and $VO_x$ over Ultra Stable Y zeolite (USY) (acidic in nature) calcined at 300 °C for 3 h showed conversion in just 10 min and 50 min, respectively, and have been reported as potential alternates to homogeneous catalysts for esterification. Presence of water had a positive influence at the start of the reaction and negative influence later when the reaction proceeds further and thus lowers the final conversion [78]. A lower calcination temperature of 450 °C instead of the commonly used temperature of 550 °C has proved to be optimum for transesterification of oleic acid as feedstock using HBeta-400 and HBeta-550 zeolite. Calcination temperature beyond 500 °C resulted in decreased conversion. Addition of a small amount of water (i.e. 2–5 wt.% of fatty acids) has been found to promote the conversion of fatty acids to biodiesel. However, further increase of the water content resulted in loss of catalytic activity [79]. Table 5 summarizes zeolite-based catalysts used for development of biodiesel.

## 7. Biodiesel synthesis by supercritical process

Biodiesel may be synthesized in supercritical process with catalyst free reaction conducted at high temperature and high pressure conditions. The process provide advantages such as improved phase solubility, overcomes mass transfer limitations, high reaction rate, easy separation and purification of the synthesized products. The process may be carried out even in the presence of moisture and FFA. However, its application in large scale production is limited by high cost involved because of high temperature and pressure, and involving a high alcohol to oil molar ratio. Madras et al. [80] synthesized biodiesel in temperature range (200–400 °C), pressure of 200 bar, and alcohol to oil molar ratio of 40:1. Almost complete conversion was observed in such supercritical conditions in 40 min of reaction time with methanol as well as ethanol. Supercritical carbon dioxide has been tried as an alternate of supercritical alcohol because of non-toxic nature of the former [81]. However, the maximum conversion obtained was less than 70% even after 5 h of reaction time with supercritical carbon dioxide in comparison to complete conversion obtained by supercritical alcohol. Bertoldi et al. [82] studied the effect of carbon dioxide as a cosolvent for synthesis of biodiesel in supercritical ethanol. A continuous tubular reactor was used and a moderate yield (37%) was obtained at optimized reaction conditions (350 °C, 10 MPa, 40:1 ethanol to oil molar ratio, and $CO_2$ to substrate mass ratio of 0.05:1 in 1 h. Almost similar yield (35%) was obtained without addition of $CO_2$ as cosolvent. Further increasing $CO_2$ to substrate mass ratio (i.e. 0.15:1, 0.3:1, and 0.5:1) decreased the yield of biodiesel. The reason attributed is low solubility of $CO_2$ in oil and high solubility in ethanol. This might have caused drawing of ethanol by

**Table 5**
Zeolites as heterogeneous catalysts.

| Heterogeneous catalyst | Calcination | | Reaction conditions | | | Conversion (*C*)/yield (*Y*) (%) | References |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | Time (h) | Molar ratio (methanol to oil) | Reaction time (h), temperature (°C) | Catalyst amount (wt.%) | | |
| ETS-10 | 500 | 4 | 6:1 | 24, 120–150 | – | $C > 90$ | 74 |
| $NaO_x$/NaX | | | | | | | |
| NaX/KOH | 120 | 3 | 10:1 | 8, 65 | 3 | $C = 85.6$ | 75 |
| Zeolites (mordenite, beta, and X) | 550 | 15 | – | –, 60 | – | $C = 93.5–95.1$ | 76 |

the cosolvent, $CO_2$, from the oil phase thus decreasing the availability of ethanol for reaction with vegetable oil.

Owing to high boiling point, a non-polar co-solvent, i.e. heptane has been tried by Tan et al. [83] to study synthesis of biodiesel by supercritical methanol. The optimum condition without a co-solvent was observed at 360 °C and 22 MPa to obtain a yield of 80%. With heptane as co-solvent 66% of yield was achieved at 280 °C. However, the yield without the co-solvent at 280 °C has not been reported which could have provided a better comparison for application with and without the co-solvent. Transesterification in supercritical condition (300–400 °C, 41.1 MPa) of a low cost feedstock, i.e. chicken fat has been tried by Marulanda et al. [84]. A low molar ratio of 6:1 (alcohol to oil) was found to be optimum for the completion of reaction in only 4–6 min. Another advantage of the process was thermally decomposition of glycerol to low molecular weight esters, ethers and hydrocarbons on reaction with methanol. Formation of these products enhanced the fuel property such as viscosity and cold flow properties. The process was also observed to be non-reversible.

## 8. Conclusion

The review indicates a growing interest in the development of heterogeneous catalyst. The emphasis laid on the application of heterogeneous catalyst is mainly to overcome the limitation incurred by homogeneous one. These limitations were mainly: separation of catalyst from reaction mixture, large amount of water generated during washing stage. However, most of the catalysts listed in the review require comparatively longer time duration while some of them need higher temperature conditions. Modification of the catalyst by an additional step, i.e. calcination at high temperature also makes the process energy intensive. Calcination leads to transformation of the origination compound to a new compound that posses catalytic-active species. Calcination also enhances the basicity, pore size, and pore volume of the catalyst. This is evidenced from MgO as catalyst which initially did not showed catalytic activity, but after its modification (calcination, etc.), a high yield and conversion was obtained.

With oxides of calcium, magnesium, and strontium as catalyst modification by calcination was needed. However, moderate reaction conditions led to almost complete conversion and a high yield. Among the oxides, CaO was found to be reused for quite a large number of times (e.g. 20 runs) which is significant in economic point of view. Using mixed oxides as catalyst, moderate conversion and yield was obtained and hence oxides of calcium and magnesium are preferable over these catalysts. CaO was also found to be resistant to some amount of water/moisture in the reactant mixture which will reduce the pretreatment cost of feedstock and alcohol.

Hydrotalcite/layered double hydroxide when used as heterogeneous catalysts also gave high conversion and yield. However, most of these catalyst required high temperature (100–200 °C) for synthesis of biodiesel and are thus energy intensive. Most of these catalysts also employed a high molar ratio which will result in high consumption of methanol, a toxic solvent.

Alumina loaded with various compound have been tried as catalyst and have shown varying results. Alumina loaded with $KNO_3$ and $Eu_2O_3$ have shown conversion less than 90%, whereas alumina loaded KF and KOH has shown high yield of 90–91%. On contrary $KI/Al_2O_3$ has shown a high conversion of 96% and is near to the specification of EN 96.5%). Zeolites have shown conversion ranging from 85% to 95% and have taken longer reaction time for completion of reaction and thus will need further modification for a higher yield and conversion to meet the international specifications.

Various heterogeneous catalysts resulted in conversion less than the minimum value (96.5%) prescribed by the European norm and hence will find little applicability at industrial level of production. New materials have been tested for their applicability as a potential heterogeneous catalyst. More of the feedstock tried for transesterification reaction has been from the edible feedstock (sunflower, soybean, etc.) which have low acid value. Only few studies have been conducted for transesterification reaction with non-edible oil, waste cooking oil, and algae which are the future feedstock. Hence the compatibility of heterogeneous catalysts with these feedstocks should be done extensively. As a potential catalyst, waste materials (egg shell) have also been successfully used as heterogeneous catalyst. Catalysts synthesized from waste material will certainly make the process cost effective and will also manage the waste product. More of such type of catalysts will certainly make the process green and sustainable in future. Nevertheless, higher conversion and yield of biodiesel obtained from the heterogeneous catalyst comparable with that of the homogeneous catalyst makes the former an upcoming catalyst for the future in biodiesel development. Reuse of the heterogeneous catalyst is another important aspect which makes it economic and preferable over the homogeneous one. However, the catalyst got deactivated in most of the catalysts utilized for transesterification and had to be reactivated by calcination or dosing with compounds. Even after reactivation, there is a limited run for which a catalyst worked and had to be discarded. Many of the heterogeneous catalysts suffered from some limitations such as low activity, and leaching which are being tried to overcome and further research are going to make these catalysts more specific and selective towards the transesterification and applicable for application at industrial level of production.

The energy efficiency and cost aspect of biodiesel is a very important aspect and has to be dealt exhaustively for a catalyst. This has been dealt to some extent in the review paper by examining the calcination temperature and time, reaction conditions (molar ratio, time, temperature, and the type and amount to catalyst used). This is a general assumption and does not necessarily be used for comparison of catalyst to be suitable in industrial point of view. A technique that utilizes supercritical conditions has gained attention for the synthesis of biodiesel where the catalyst is generally not added. A high temperature, pressure, and alcohol volume is needed which makes the process costly. However, the process is tolerant to high FFA and water contents in the feedstock and the reaction gets completed in comparatively shorter time duration.

## Acknowledgements

The authors gratefully acknowledge the financial assistance to Bhaskar Singh by Council of Scientific & Industrial Research (CSIR), New Delhi, India, in form of Senior Research Fellowship (SRF).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2010.10.015.

## References

[1] Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. Appl Catal A: Gen 2009;363:1–10.

[2] Di Serio D, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.

[3] Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: a review. Fuel Process Technol 2009;90:770–7.

[4] Vicente G, Coteron A, Martinez M, Aracil J. Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. Ind Crops Prod 1998;8:29–35.

[5] López DE, Goodwin Jr JG, Bruce DA, Lotero E. Transesterification of triacetin with methanol on solid acid and base catalysts. Appl Catal A: Gen 2005;295:97–105.

[6] Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind Eng Chem Res 2006;45:3009–14. In Di Serio D, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.

[7] Dossin TF, Reyniers MF, Berger RJ, Marin GB. Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. Appl Catal B: Environ 2006;67:136–48.

[8] Dossin TF, Reyniers MF, Marin GB. Kinetics of heterogeneously MgO-catalyzed transesterification. Appl Catal B: Environ 2006;62:35–45.

[9] Tateno T, Sasaki T. Process for producing fatty acid fuels comprising fatty acids esters. US Patent 6818,026, Nov 16, 2004. In Serio MD, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.

[10] Li E, Rudolph V. Transesterification of vegetable oil to biodiesel over MgO-functionalized mesoporous catalysts. Energy Fuels 2008;22:145–9.

[11] Ilgen O, Akin AN. Transesterification of canola oil to biodiesel using MgO Loaded with KOH as a heterogeneous catalyst. Energy Fuels 2009;23:1786–9.

[12] Liang X, Gao S, Wu H, Yang J. Highly efficient procedure for the synthesis of biodiesel from soybean oil. Fuel Process Technol 2009;90:701–4.

[13] Wang L, Yang J. Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. Fuel 2007;86:328–33.

[14] Wang Y, Zhang F, Xu S, Yang L, Li D, Evans DG, et al. Preparation of macrospherical magnesia-rich magnesium aluminate spinel catalysts for methanolysis of soybean oil. Chem Eng Sci 2008;63:4306–12.

[15] Huaping Z, Zongbin W, Yuanxiong C, Ping Z, Shijie D, Xiaohua L, et al. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. Chin J Catal 2006;27:391–6.

[16] Granados ML, Poves MDZ, Alonso DM, Mariscal R, Galisteo FC, Tost RM, et al. Biodiesel from sunflower oil by using activated calcium oxide. Appl Catal B: Environ 2007;73:317–26.

[17] Veljkovic VB, Stamenkovic OS, Todorovic ZB, Lazic ML, Skala DU. Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. Fuel 2009;88:1554–62.

[18] Kouzu M, Kasuno T, Tajika M, Yamanaka S, Hidaka J. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. Appl Catal A: Gen 2008;334:357–65.

[19] Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel 2008;87:216–21.

[20] Albuquerque MCG, Urbistondo IJ, González JS, Roble JMM, Tost RM, Castellón ER, et al. CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. Appl Catal A: Gen 2008;334:35–43.

[21] MacLeod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.

[22] Watkins RS, Lee AF, Wilson K. Li–CaO catalysed tri-glyceride transesterification for biodiesel applications. Green Chem 2004;6:335–40.

[23] Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresour Technol 2009;100:696–700.

[24] Demirbas A. Biodiesel from sunflower oil in supercritical methanol with calcium oxide. Energy Convers Manage 2007;48:937–41.

[25] Granados ML, Alonso DM, Sadaba I, Mariscal R, Ocon P. Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: the case of triglycerides methanolysis using CaO. Appl Catal B: Environ 2009;89:265–72.

[26] Yan S, Kim M, Salley SO, Ng KYS. Oil transesterification over calcium oxides modified with lanthanum. Appl Catal A: Gen 2009;360:163–70.

[27] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresour Technol 2009;100:2883–5.

[28] Ngamcharussrivichai C, Wiwatnimit W, Wangnoi S. Modified dolomites as catalysts for palm kernel oil transesterification. J Mol Catal A: Chem 2007;276:24–33.

[29] Sakai T, Kawashima A, Koshikawa T. Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. Bioresour Technol 2009;100:3268–76.

[30] Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 2007;8:1107–11.

[31] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catal Today 2005;106:190–2.

[32] Yang Z, Xie W. Soybean oil transesterification over zinc oxide modified with alkali earth metals. Fuel Process Technol 2007;88:631–8.

[33] Liu X, Piao X, Wang Y, Zhu S, He H. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. Fuel 2008;87:1076–82.

[34] Martyanov IN, Sayari A. Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium, and calcium methoxides. Appl Catal A: Gen 2008;339:45–52.

[35] Kawashima A, Matsubara K, Honda K. Development of heterogeneous base catalysts for biodiesel production. Bioresour Technol 2008;99:3439–43.

[36] Ngamcharussrivichai C, Totarat P, Bunyakiat K. Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. Appl Catal A: Gen 2008;341:77–85.

[37] McNeff CV, McNeff LC, Yan B, Nowlan DT, Rasmussen M, Gyberg AE, et al. A continuous catalytic system for biodiesel production. Appl Catal A: Gen 2008;343:39–48.

[38] Albuquerque MCG, Santamaria-González J, Mérida-Robles JM, Moreno-Tost R, Rodríguez-Castellón E, Jiménez-López A, et al. MgM (M = Al and Ca) oxides as basic catalysts in transesterification processes. Appl Catal A: Gen 2008;347:162–8.

[39] Fraile JM, Garcia N, Mayoral JA, Pires E, Roldan L. The influence of alkaline metals on the strong basicity of Mg–Al mixed oxides: the case of transesterification reactions. Appl Catal A: Gen 2009;364:87–94.

[40] Bejoy N. Hydrotalcite the clay that cures. Resonance 2001;6:57–61.

[41] Siano D, Nastasi M, Santacesaria E, Di Serio M, Tesser R, Minutillo G, et al. Process for producing esters from vegetable oils and animal fats by using heterogeneous catalysts. WO 050925 A1 (2006). In Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: a review. Fuel Process Technol 2009;90:770–7.

[42] Cantrell DG, Gillie LJ, Lee AF, Wilson K. Structure–reactivity correlations in MgAl hydrotalcite catalysts for biodiesel synthesis. Appl Catal A: Gen 2005;287:183–90.

[43] Xie W, Peng H, Chen L. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. J Mol Catal A: Chem 2006;246:24–32.

[44] Liu Y, Lotero E, Goodwin Jr JG, Mo X. Transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. Appl Catal A: Gen 2007;331:138–48.

[45] Yagiz F, Kazan D, Akin AN. Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. Chem Eng J 2007;134:262–7.

[46] Hernandez MR, Labarta JAR, Valdes FJ. New heterogeneous catalytic transesterification of vegetable and used frying oil. Ind Eng Chem Res 2010;49:9068–76.

[47] Jiang W, Lu H, Qi T, Yan S, Liang B. Preparation, application, and optimization of Zn/Al complex oxides for biodiesel production under sub-critical conditions. Biotechnol Adv 2010;28:620–7.

[48] Zeng H, Liao K, Deng X, Jiang H, Zhang F. Characterization of the lipase immobilized on Mg–Al hydrotalcite for biodiesel. Process Biochem 2009;44:791–8.

[49] Barakos N, Pasias S, Papayannakos N. Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst. Bioresour Technol 2008;99:5037–42.

[50] Zeng H, Feng Z, Deng X, Li Y. Activation of Mg–Al hydrotalcite catalysts for transesterification of rape oil. Fuel 2008;87:3071–6.

[51] Trakarnpruk W, Porntangjitlikit S. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renew Energy 2008;33:1558–63.

[52] Gao L, Xu B, Xiao G, Lv J. Transesterification of palm oil with methanol to biodiesel over a KF/hydrotalcite solid catalyst. Energy Fuels 2008;22:3531–5.

[53] Gao L, Teng G, Xiao G, Wei R. Biodiesel from palm oil via loading KF/Ca–Al hydrotalcite catalyst. Biomass Bioenergy 2010;34:1283–8.

[54] Antunes WM, Veloso CO, Henriques CA. Transesterification of soybean oil with methanol catalyzed by basic solids. Catal Today 2008;133–135:548–54.

[55] Guerreiro L, Pereira PM, Fonseca IM, Aranda RMM, Ramos AM, et al. PVA embedded hydrotalcite membranes as basic catalysts for biodiesel synthesis by soybean oil methanolysis. Catal Today 2010;156:191–7.

[56] Cordeiro CS, Arizaga GGC, Ramos LP, Wypych F. A new zinc hydroxide nitrate heterogeneous catalyst for the esterification of free fatty acids and the transesterification of vegetable oils. Catal Commun 2008;9:2140–3.

[57] Li E, Xu ZP, Rudolph V. MgCoAl–LDH derived heterogeneous catalysts for the ethanol transesterification of canola oil to biodiesel. Appl Catal B: Environ 2009;88:42–9.

[58] Shumaker JL, Crofcheck C, Tackett SA, Jimenez ES, Morgan T, Ji Y, et al. Biodiesel synthesis using calcined layered double hydroxide catalysts. Appl Catal B: Environ 2008;82:120–30.

[59] Sun H, Hu K, Lou H, Zheng X. Biodiesel production from transesterification of rapeseed oil using KF/$Eu_2O_3$ as a catalyst. Energy Fuels 2008;22:2756–60.

[60] Lacome T, Hillion G, Delfort B, Revel R, Leporq S, Acakpo G. Process for transesterification of vegetable or animal oils using heterogeneous catalysts based on titanium, zirconium or antimony and aluminium. US Patent Application No US 2005/0266139, Dec 1, 2005. In Serio MD, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.

[61] Kim HJ, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, et al. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catal Today 2004;93–95:315–20.

[62] Ebiura T, Echizen T, Ishikawa A, Murai K, Baba T. Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid-base catalyst. Appl Catal A: Gen 2005;283:111–6.

[63] Xie W, Peng H, Chen L. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. Appl Catal A: Gen 2006;300:67–74.

[64] Vyas AP, Subrahmanyam N, Patel PA. Production of biodiesel through transesterification of Jatropha oil using $KNO_3/Al_2O_3$ solid catalyst. Fuel 2008;88:625–8.

[65] Xie W, Li H. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J Mol Catal A: Chem 2006;255:1–9.

[66] Arzamendi G, Campoa I, Arguiñarena E, Sánchez M, Montes M, Gandía LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. Chem Eng J 2007;134:123–30.

[67] Li X, Lu G, Guo Y, Wang Y, Zhang Z, Liu X, et al. A novel solid superbase of $Eu_2O_3/Al_2O_3$ and its catalytic performance for the transesterification of soybean oil to biodiesel. Catal Commun 2007;8:1969–72.

[68] Alonso DM, Mariscal R, Tost RM, Poves MDZ, Granados ML. Potassium leaching during triglyceride transesterification using $K/\gamma$-$Al_2O_3$ catalysts. Catal Commun 2007;8:2074–80.

[69] Bo X, Guomin X, Lingfeng C, Ruiping W, Lijing G. Transesterification of palm oil with methanol to biodiesel over a $KF/Al_2O_3$ heterogeneous base catalyst. Energy Fuels 2007;21:3109–12.

[70] Noiroj K, Intarapong P, Leungnaruemitchai A, In SJ. A comparative study of $KOH/Al_2O_3$ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renewable Energy 2009;34:1145–50.

[71] Benjapornkulaphong S, Ngamcharussrivichai C, Bunyakiat K. $Al_2O_3$-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil. Chem Eng J 2009;145:468–74.

[72] Umdu ES, Tuncer M, Seker E. Transesterification of *Nannochloropsis oculata* microalga's lipid to biodiesel on $Al_2O_3$ supported CaO and MgO catalysts. Bioresour Technol 2009;100:2828–31.

[73] Rongxian B, Yisheng T, Yizhuo H. Study on the carbon dioxide hydrogenation to iso-alkanes over Fe–Zn–M/zeolite composite catalysts. Fuel Process Technol 2004;86:293–301.

[74] Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ. Transesterification of soybean oil with zeolite and metal catalysts. Appl Catal A: Gen 2004;257:213–23.

[75] Xie W, Huang X, Li H. Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. Bioresour Technol 2007;98:936–9.

[76] Ramos MJ, Casas A, Rodríguez L, Romero R, Pérez A. Transesterification of sunflower oil over zeolites using different metal loading: a case of leaching and agglomeration studies. Appl Catal A: Gen 2008;346:79–85.

[77] Brito A, Borges ME, Otero N. Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil. Energy Fuels 2007;21: 3280–3.

[78] Marchetti JM, Errazu AF. Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid. Fuel 2008;87:3477–80.

[79] Ha L, Mao J, Zhou J, Zhang ZC, Zhang S. Skeletal isomerization of unsaturated fatty acids on Beta zeolites: effects of calcination temperature and additives. Appl Catal A: Gen 2008;356:52–6.

[80] Madras G, Kolluru C, Kumar R. Synthesis of biodiesel in supercritical fluids. Fuel 2004;83:2029–33.

[81] Rathore V, Madras G. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide. Fuel 2007;86:2650–9.

[82] Bertoldi C, Silva C, Bernardon JP, Corazza ML, Filho LC, Oliveira JV, et al. Continuous production of biodiesel from soybean oil in supercritical ethanol and carbon dioxide as cosolvent. Energy Fuels 2009;23:5165–72.

[83] Tan KT, Lee KT, Mohamed AR. Effects of free fatty acids, water content and co-solvent on biodiesel production by supercritical methanol reaction. J Supercrit Fluids 2010;53:88–91.

[84] Marulanda VF, Anitescu G, Tavlarides LT. Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. J Supercrit Fluids 2010;54:53–60.