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Review of Catalytic Transesterification Methods for Biodiesel Production

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Abstract

Attempts for improving the synthesis procedure of catalysts for fatty acid methyl ester production have been progressing for a considerable length of time. Biodiesel lessens net carbon dioxide emissions up to 78% with reference to conventional fuel. That is the reason for the improvement of new and operative solid catalysts necessary for inexhaustible and efficient fuel production. Homogenous base catalysts for transesterification is risky in light of the fact that it produces soap as byproduct, which makes difficult issues like product separation and not temperate for industrial application. In comparison, heterogeneous process gives higher quality FAME which can be effectively isolated and facilitate costly refining operations that are not required. A focus of this review article is to study and compare various biodiesel synthesis techniques that are being researched. The catalytic strength of numerous heterogeneous solid catalysts (acid and base), specially earth and transition metal oxides were also appraised. It was observed that catalytic proficiency relied upon a few factors, for example, specific surface area, pore size, volume and active site concentration at catalyst surface. This review article will give assistance in assortment of appropriate catalysts and the ideal conditions for biodiesel generation.

Keywords: biodiesel, heterogeneous catalyst, fatty acid methyl ester, transition metals, vegetable oil, transesterification

1. Introduction

Fatty acid methyl ester (FAME) commonly called biodiesel is a fuel derived from renewable sources suitable for use in conventional compression-ignition engines. The interest and

development of biofuels has grown exponentially over the last few years in response to the need to develop sustainable energy resources and to address climate change. Currently, biodiesels are the most successful fossil fuel supplements. Notwithstanding limited market share, biodiesel has several strong traits to make a considerable influence to energy portfolio propose that its usage will continue to raise in the forthcoming years. Many countries are promoting the use of biodiesel through government incentives and targets, and the production of biodiesel is increasing worldwide. Besides the obvious economic benefits, renewable fuels are also offering environmental benefits by reducing the greenhouse gas emission and increase the energy security of the country by plummeting necessity on foreign oil.

FAME is synthesized through the transesterification reaction of triglyceride and methanol. Transesterification is the process by which an ester is converted into another product over the exchange of the alkoxy moiety.

Vegetable oils are attractive promising substitute to diesel fuel since they are inexhaustible in nature and can be produced locally and eco-friendly as well. All unsaturated fat sources, such as animal fats or plant lipids can be used in biodiesel production [1–5]. Edible vegetable oils like canola, soybean and corn have been utilized for biodiesel generation and observed to be great as a diesel substitute [6, 7]. The non-consumable vegetable oils such as *Madhuca indica*, *Jatropha curcas* and *Pongamia pinnata* are observed to be suitable for biodiesel synthesis under the test conditions researched. In perspective of the few focal points, vegetable oils have an incredible potential to supplant oil-based powers over the long haul [7–9].

2. Transesterification methods

Catalysis of transesterification can be done by catalytic, non-catalytic and enzymatic [8–11]. Non-catalytic transesterification mechanism takes place at supercritical conditions. These conditions entail a greater temperature and higher pressure, which is not an economically viable choice, for this reason catalytic transesterification approaches for biodiesel production are more commonly used and more vastly preferred [12]. Homogeneous catalysis may be basic, acidic or enzymatic in which basic catalysis of oils comprise alkaline, for example, potassium and sodium hydroxide, alkoxides summary of catalytic methods are given in **Figure 1**. At low temperature and pressure, basic catalysts have extraordinary activity rate in transesterification. Sulfuric, hydrochloric and sulfonic acids are the major acid catalysts [13, 14]; whereas homogeneous acids and bases have well-defined chemical properties; heterogeneous acid and bases exhibit a variety of sites; while heterogeneous catalysts can be categorized by the Bronsted or Lewis nature of sites, acid or base strength of sites and the texture of support [15, 16].

The base catalyzed transesterification process is primary viable heterogeneous process practiced now a days [11]. It has various mechanism which converts the triglycerides (TG) to FAME with the liberation of glycerol such as a byproduct [17, 18]. Specialists are seeking after new catalyst. Additionally, the limpiness of the required feedstock, reaction kinetics and postreaction processing is relying on the used catalyst [19].

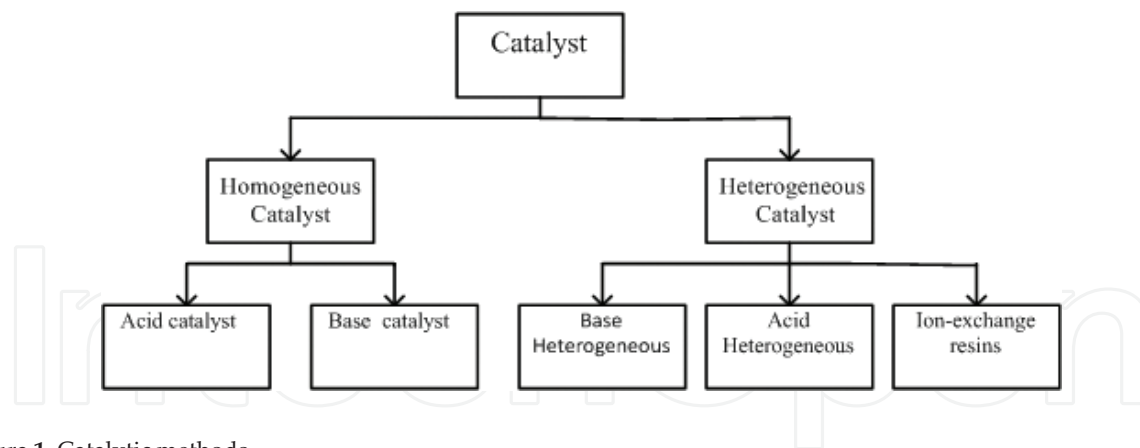


Figure 1. Catalytic methods.

3. Heterogeneous versus homogenous catalysis

Catalyst fundamentally has a place with the classifications of homogeneous or heterogeneous. Homogeneous catalyst act in a soluble stage from the blend, while heterogeneous catalyst act in an alternate stage from the response blend. The outline of reactant process is given in **Figure 2**. Being in an alternate stage, heterogeneous impetuses have the upside of simple partition and reuse [17].

Heterogeneous catalyst is supplanting homogeneous catalyst because of hurdles in catalyst separation and waste disposal. [18]. The need for the neutralization step and subsequent disposal of neutralized salt in acid and base catalyzed reactions could be eliminated by replacing

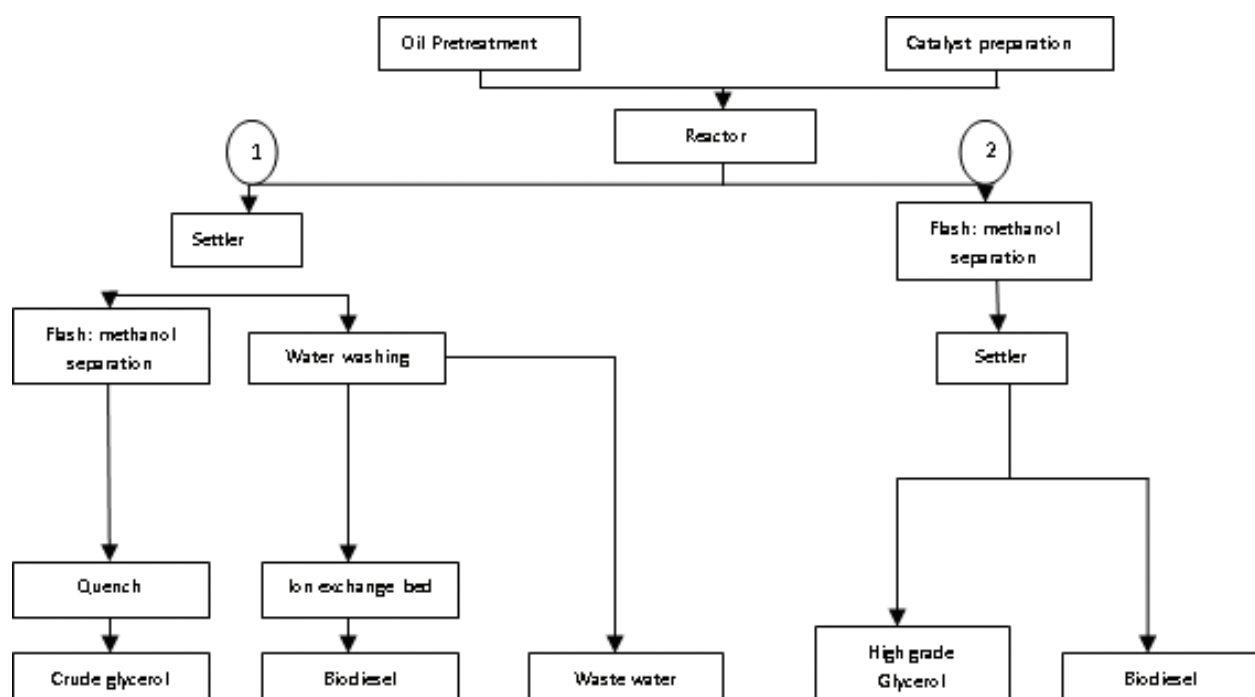


Figure 2. Biodiesel production path way by heterogeneous and homogeneous process.

a homogeneous acid or base by a heterogeneous catalyst. This trend to switch homogeneous catalysts with heterogeneous catalysts is part of the drive toward green chemistry which in turn minimize waste and eliminate the need for harmful reactants. Comparison of catalysis for biodiesel production is given in **Table 1** which reveals that many industrial processes now operate with solid acid catalysts [19]. But fewer processes operate with solid bases, as solid bases are less prevalent than solid acids [20].

Type	Homogeneous catalysts	Enzymatic catalysts	Heterogeneous catalysts
Advantage	<p>Modest operation conditions</p> <p>Base catalyst give favourable kinetics: high activity and give high yield in short time</p> <p>Base catalysts are 4000 times faster reaction than acid catalyzed transesterification</p> <p>Basic methoxides are more effective than hydroxides</p> <p>Acid catalysts can be used for both esterification and transesterification simultaneously</p> <p>Acid catalyst are preferred for low grade oils and are insensitive to FFA and water</p>	<p>Very selective</p> <p>FFA are converted to biodiesel</p> <p>Low reaction temperature, insensitive to water</p> <p>Ease of separation products</p> <p>Higher yield than base catalysts</p> <p>Can be implemented as homogeneous or heterogeneous catalysts</p>	<p>Environmentally benign, noncorrosive, recyclable, fewer disposal problems</p> <p>Ease separation of products, higher selectivity, longer catalyst life</p> <p>Acid heterogeneous catalyze both esterification and transesterification simultaneously and insensitive to FFA and water</p> <p>Comparatively cheap</p> <p>Can be used in continuous fixed bed reactors</p>
Disadvantages	<p>Separation of waste problem after reaction</p> <p>Saponification, emulsion formation</p> <p>Catalyst reuse not possible</p> <p>Limited to batch type of reactors</p> <p>Basic catalysts are sensitive to the presence of FFA and water</p> <p>High production cost compared with heterogeneous type</p> <p>Acid catalysts are corrosive and give very small reaction rate</p> <p>Acid catalysts require higher molar ratio of methanol to oil, higher temperature, concentration acid and more waste from neutralization reaction</p>	<p>Expensive</p> <p>Enzyme is inhibited in the presence of methanol and may require additional supportive solvents to be used as a medium</p>	<p>Currently moderate conversion compare to high active basic homogeneous</p> <p>Mass transfer limitation due to the presence of three phase and need well mixing</p> <p>Basic catalysts require low FFA and anhydrous condition and pretreatments is required for high FFA feedstock</p> <p>High alcohol to oil ratio required, high temperature and pressure</p> <p>Acidic catalysts: low acid site concentration, low microporosity, and high cost compared with basic types</p>
References	[17, 24–27]	[13, 17, 25, 28, 29]	[13, 17, 24, 30–33]

Table 1. Comparison of homogeneous, heterogeneous and enzymatic catalysis for biodiesel production.

The homogeneous catalysts, commonly utilized for commercial processes, have some disadvantages, such as they cannot recycle, large amounts of waste water is being produced, produce low grade glycerol as byproduct. In other hand, the heterogeneous catalysis offers easy production and purification process with reference to economic and environment. Truth is told, a few scientists have announced the potential monetary focal points of the heterogeneous reactant process over the option homogeneous one [21–23].

Cost of biodiesel production by heterogeneous catalysts is 4–20% less than homogeneous catalysts. Preparation of new long-lasting heterogeneous catalysts with anticipated physical and chemical properties is one of the most important and eye-attracting emphases of the latest studies. This is the main reason for the production of new heterogeneous catalysts which are suitable for pure biodiesel from different type of fatty acids that have been produced and appraised for FAME synthesis processes [24–26].

However, numerous additional thought-provoking issues endure to be resolved until highly proficient solid catalysts can be industrialized. However, with a specific end goal to build up a superior comprehension of impetus outline for the transesterification procedure, distinctive heterogeneous incentive utilized for biodiesel generation has been considered and examined in this article. It can be concluded that each of these catalyst properties have remarkable effect on the transesterification reaction. The application of catalysts is for various kinds of oils, reaction parameters and there for stability of the catalysts are also incorporated in this discussion. It can be inferred that each of these catalyst properties have significant influences on the transesterification process.

4. Biodiesel production with alkaline metal oxides and derivatives

4.1. Acid catalyzed transesterification

Homogeneous Lewis acid (H_2SO_4) and carboxylates (PbCH_3COOH) have been used as catalyst for biodiesel production from oil even if it have high concentration of FFA [13, 27, 28]. Several heterogeneous acids were also used and reported in literature (ion-exchange resin, metal oxides, heteropolyacids, etc.). However, three main drawbacks reported for the use of carboxylates catalyst are its work under high temperature and pressure ($T > 190^\circ\text{C}$, $P > 20$ bar); purification of product is costly and not economical for industrial application. Supported sodium and potassium on larger surface area zeolite and alumina had given upto 85% conversion of fame which is still lower as compare to solid base catalyst [6, 29, 30].

4.2. Base catalyzed transesterification

Presently, there are various alkali-based catalysts have been utilized as homogeneous and heterogeneous transesterification. Base catalyzed transesterification is substantially less time consuming with respect to acid catalyzed transesterification and it is regularly used technique for commercial purpose. Numerous solid alkali base metal oxides and there substrate have

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Li/CaO	3	60	100	[87]
Li-Al HTA	1	65	83	[88]
LiNO ₃ /Al ₂ O ₃	1	60	91.6	[90]
H ₂ SO ₄ :NaOH	6	60	96.4	[39]
NaOH	1	60	97	[79]
Na/NaOH/ γ -Al ₂ O ₃	1	25–65	89	[85]
KOH/NaY	3	60	91.1	[64]
Na/NaOH	1	60	70	[91]
NaOH/Al ₂ O ₃	2	60	65	[91]
NaNO ₃ /Al ₂ O ₃	4	60	24.7	[90]
NaO/NaX	1	65	28	[85]
Ki/NaX	2	65	12.9	[6]
Al ₂ O ₃ /Na/NaOH	2	60	83	[91]
KI/SiO	8	70	90.9	[47]
KNO ₃ /Al ₂ O ₃	6	65	84	[26]
K ₂ CO ₃ /MgO	2	70	99	[26]
KAlSiO ₄ doped in Li	2 min	120	100	[92]
KOH/MgO	7	100	99.4	[93]
KNO ₃ /Al ₂ O ₃	7	70	87	[47]
KI/Al ₂ O ₃	3	60	96	[47]
KF/Al ₂ O ₃	3	65	90	[66]
KOH/Al ₂ O ₃	2	60	91.1	[60]
KCO ₃ /Al ₂ O ₃	5	65	48	[47]
KNO ₃ /Al ₂ O ₃	5	65	84–87	[94]
KOH/Al ₂ O ₃		65	80.2	[47]
KOH/NaX		60	82	[85]
KX		60	82	[85]
KI/ZnO		60	72.6	[47]
Kf/ZnO		60	80	[47]
Ki/ZrO		60	78.2	[47]
Al ₂ O ₃ /KNO ₃	7	60	83	[47]
Al ₂ O ₃ /KI	8		96	[16]
ZnO/KF	9	65	87	[47]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
ZnO/Ba	1	65	95	[47]
Na/hydrotalcite with pure oil	8	60	88	[90]
Na/hydrotalcite with used oil	8	60	67	[90]
KF/hydrotalcite	5	65	92	[76]
KF/Ca–Al hydrotalcite	3	65	99	[77]

Table 2. Alkaline metal oxides catalysts used for the transesterification of oils.

been used for homogeneous catalyzed transesterification (**Table 2**). The benefit of alkali base catalysis requires a little amount in catalysis [8].

Basic metal alkoxide, hydroxide and sodium and potassium carbonates are utilized as a part of alkali-based catalyzed transesterification process [31–37]. With virgin vegetable oil, basic catalyst typically show high performance. If oil have critical amount of unsaturated fats then these free unsaturated fats respond with the basic catalyst to produce soap that inhibit glycerol that restrain the division of biodiesel, glycerin and wash water [16, 38]. NaOH or KOH are generally utilized as catalyst for transesterification of triglycerides at atmospheric pressure and temperature. Evacuation of these catalyst is in fact troublesome and it adds additional cost to the final product [39, 40]. It was reported in may researches that alkaline metal are less expensive than metal alkoxides, however the action of alkaline metal alkoxides (CH_3ONa for the methanolysis) is more dynamic as catalyst, then soluble metal hydroxides (KOH and NaOH since the previous) give high yield in short time than the last mentioned.

Homogeneous base catalyst catalyzed transesterification of oil into FAME fast. Freedman et al. observed that only 1% sodium hydroxide gives 94% conversion of oil at the temperature of 333 K for 0.1 h. The reaction is very vigorous between a plant oil and CH_3NaO , when alcohol is being used as solvent. It takes 2–3 min for complete transesterification of triglycerides at room temperature (293–298 K) by using CH_3NaO as catalyzed. While if we use homogeneous acid and base for transesterification, it takes 60–360 min at 303–338 K. Freedman et al. stated that only 1% sodium hydroxide gives about 94% of FAME [41–45].

However, water which is produced as byproduct caused during soap formation, as a result it becomes hard to recover catalyst and purification the products. Therefore, NaOH and KOH catalysts become slowly got replaced in coming eras by environmental friendly and long-lasting heterogeneous catalysts. However, these catalysts exhibit remarkable activity in esterification of FFA, but on the other hand they are not good in glycerides transesterification. Moreover a huge number of these catalysts get leached into product [46, 47]. In lot of cases, catalyst undergo fouling due to impurities in reaction mixture [48, 49].

Now a days, alkali oxides, alkaline oxide earth metals supported over large surface area are used for biodiesel production [50].

It was reported that alkaline metal are economical than metal alkoxides, but the activity of alkaline metal alkoxides (CH_3ONa for the methanolysis) is higher than KOH and NaOH , since the former gives high yield in short reaction time than the latter. In industries, biodiesel is synthesized, now a days, by transesterification of oils in presence of solvent along with NaOH and NaOMe . The advantage of the homogeneously base catalyzed transesterification is that the reaction of transesterification is very fast and performed at room temperature. Glycerol and FAME are being separated by settling after catalyst neutralization followed by purification of crude glycerol and biodiesel [51].

However, during the transesterification reaction, certain amount of water is produced as byproduct which causes ester hydrolysis along with soap, as a result it become hard to purify product by separating the catalyst. Therefore, it is assumed that heterogeneous catalyst will replace conventional homogeneous catalysts. Homogeneous catalysts show good performances in FFA esterification, while their performance for glycerides transesterification is not suitable. Another drawback is that this catalyst leached into reaction mixture and showed rapid deactivation [66, 67]. Alkali salts supported on metal oxide such as $\text{KOH}/\text{Al}_2\text{O}_3$, KF/MgO exhibited good results for transesterification [52, 53].

Recently, numbers of heterogeneous catalysts such as ion-exchange resin CaO , alkylguanidines, $\text{KI}/\text{Al}_2\text{O}_3$, $\text{Na}/\text{NaOH}/\text{Al}_2\text{O}_3$, ionic liquid and lipase have been reported in literature for catalyzed transesterification of vegetable oils in presence of methanol [54–63].

Gao et al. prepared KF supported on hydro calcite by using co-precipitation techniques. It was observed that the formation of KMgF_3 and KAlF_4 enhance catalytic activity of catalyst. $\text{KF}/\text{hydro calcite}$ gives 92% fame yield with 12:1 (alcohol to oil) molar ratio in 5 h reaction time at 65°C .

Gao et al. also study the percentage activity of KF supported at Ca-Al hydro calcite. He observed that catalytic activity is very satisfactory, about 99.7% yield can be obtained. It was assumed that this high output of 99.74% was due to the new crystal phases KCaF_3 , KCaCO_3F and $\text{CaAl}_2\text{F}_4(\text{OH})$ [64, 65]. KI loaded at mesoporous silica has been used as heterogeneous catalysis for conversion of TG in to FAME. It was observed that increase in reaction temperature and time enhances yield up to 90.09%. This highest yield were obtained at 70°C , 15 wt.% of KI , within 8 h by using 5.0% by weight of the oil [34].

It was reported that biodiesel could be effectively produced by two-step process with ultrasonic radiation in less time. Xin deng in 2010 investigated two-step esterification and transesterification of jatropha oil in ultrasonic reactor. He used NaOH and H_2SO_4 as catalyst at 60°C the reaction temperature. It was observed that 96.4% yield can be obtain just in 1.5 h by esterification of oil with H_2SO_4 for 1 h and then subsequent transesterification by NaOH for 0.5 h [66].

Umer et al. used alkali catalyst for transesterification of sunflower oils to alkyl esters. They get 97.1% yield at 60.8°C by using 1%W catalyst. However, he observed that increase in catalyst concentration above 1 wt% has no effect at yield but it could add extra costs of production [67]. Sulfuric acid or hydrochloric acid used as homogeneous catalyst does not produce soap but the main problem in using these catalyst is corrosiveness and downstream purification

and separation of product is costly and not economical. On the other hand use of heterogeneous acid catalyst can overcome these problems and could reduce economic issues and better profitability of the biodiesel production process [68–70].

Hamed et al. reported the use of RSM response surface methodology as a statistical tool for study instruction among experimental variables and optimizing reaction condition [71]. Jeong et al. had reported 98% conversion of FAME [54]. He used RSM to study animal fat transesterification at 65°C for 20 min, KOH (1.25 wt% 7.5:1 molar ratio of methanol and fat) [72].

According to literature, the production of methyl ester with extraordinary yield not only the choice of catalyst but also experimental conditions should be concerned, optimization of some reaction parameters and the application of those parameters are essential. Solid base catalyst synthesized by loading KNO₃ aluminum oxide calcinated at 773 K for 5 h gives only 75% conversion by using 3.5% catalyst. While same method was used by Supper et al. in 2004 for preparing Na/NaOH/ γ -Al₂O₃ catalyst. Supper et al. reported high conversion of soybean oil by using 1–3% w at 25–65°C and 1–3% w/w catalyst was found to attain conversion rate that was more than two orders of magnitude [73].

Heterogeneous catalysts possessing dual acidic and basic sites had been examined which could simultaneously esterify FFA and transesterify triglycerides (TG) to biodiesel [74]. Catalytic activity of Li/CaO has been stated by Watkins et al., where 100% FAME has been achieved 3 h at 60°C [75]. Shumaker et al. reported that Li-Al HTA was found to work efficiently and gives 65% yield only in 1 h reaction time [76]. Hernandez et al. used incorporated sodium hydrotalcite in Mg–Al mixed oxide. Sodium was incorporated as sodium acetate in Mg–Al mixed oxide calcite at 500°C for 8 h. He found that incorporation of sodium enhances the activity and it works at a low temperature (60°C) and with pure and used soybean oil. This catalyst gives 88% conversion for pure soybean oil and 67% for used soybean oil [77].

5. Biodiesel production with alkaline earth metals and metalloids

Several attempts had been made in search for promising solid base alkali earth oxides catalyst such as CaO, SrO and BaO [78–81]. Magnesium oxide and salts based catalyst have been examined in past by different research. Early research has not showed satisfactory output, but far ahead on CaO and MgO were modified to acquire 99% yield and conversion of biodiesel. It was observed that preparation method, calcination and time of reaction and temperature and oil to methanol molar ratio have a great impact at biodiesel yield. Wang et al. used nano-magnesium oxide for transesterification of vegetable oil at 250°C reaction temperature for 0.3 h reported biodiesel yield was 98% [82].

MgO is very reactive at supercritical reaction condition giving up to 99% methyl ester. It was observed that reaction is finished in 10 min at 300°C by using methanol to oil molar ratio of 39.6:1. [83, 84].

Venkat Reddy et al. used noncrystalline CaO for the conversion of poultry fat triglyceride into biodiesel. He observed 100% conversion of FAME at 25°C with temperature with 1 mmol

of 1 wt% catalyst). The reaction was performed for 7 h by using 70:1 molar ratio of methanol to triglyceride [85].

Li et al. used MgO supported silica as a solid heterogeneous catalyst at 220°C for 5 h reaction time gives 96% biodiesel yield [80]. Additionally, magnesium oxide supported at high surface area metal like lanthanum, zirconium and aluminum have been screened for biodiesel production. Babu et al. reported that magnesium oxide supported at zirconium oxide showed 100% yield in 30 min just at 65°C reaction temperature [86, 87].

Furthermore, Ngamcharussrivichai et al. used $\text{CaMg}(\text{CO}_3)_2$ as a catalyst for esterification of plant oil. They remarked that under 60°C in 3 h, the catalyst yielded optimum biodiesel yield of 99.9% [88, 116]. Takagaki et al. and Li et al. studied catalytic activity of magnesium- and aluminum-based metal oxides such as Mg-Al HTA, Mg/Al/Zr, Mg/Al HT, Mg/Al and MgO/ Al_2O_3 in the methanolysis of plant oil. Batch reactor was used for reaction for different combination at 65–130°C. The reaction time was from 1 to 4 h, resulting in yield of 65–90.5%. It was observed that Mg-Al HTA show high durability, ester product more than 90.5% and can be effectively used as heterogeneous base catalysts [89–91].

Serio et al. described the kinetics of MgO heterogeneously catalyzed methanolysis of soybean oil by using MgO/ Al_2O_3 , MgO/Cao as catalyst. He observed 92% yield in the transesterification of soybean oil at 60°C within 2 h reaction time MgO/Cao catalyst [92]. Ochoa et al. and Liu et al. used CaO as heterogeneous catalyst. It was observed that when CaO was calcination at 550°C temperature, 98% yield can be obtained at 60°C within reaction temperature and in 2 h reaction time [93, 94].

Nakatani et al. had used oyster shell as CaO source. He obtained 96% conversion of fame at 65°C for 4h reaction time. While Boey et al. used mud crab shell as heterogeneous catalyst for transesterification of palm olein, the results showed 98% yield in 150 min at 65°C reflux temperature. Sarin et al. used seashell and eggshells as CaO source for TG conversion from different feed stocks. All this catalyst shows 98% FAME yield only in 60 min of reaction time [59, 95–97].

Albuquerque et al. used mesoporous silica supported by CaO as solid base catalyst for biodiesel production and gets 95% conversion in 5 h reaction at 60°C reaction temperature [98].

$\text{CaMg}(\text{CO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2/\text{Al}_2\text{O}_3$ were used as solid base catalyst by Ngamcharussrivichai et al., Benjapornkulaphong et al., for palm kernel oil transesterification at 60°C reaction temperature. They get 99.9 and 94% yield, respectively, after 3 h reaction time [26, 88]. Summary of alkaline earth metals and metalloids is given in **Table 3**.

Kouzu et al. [98] investigated the use of CaO as catalyst in a batch reactor at methanol reflux temperature for 2 h and achieved 93% biodiesel production. Kawashima et al. also discussed calcium oxide activity as catalyst along with its derivatives such as $\text{Ca}(\text{OCH}_3)_2$, CaTiO_3 , CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaZrO_3 and CaO-CeO_2 for rapeseed oil transesterification of rapeseed oil. CaO were activated by methanol at 25°C for 1.5 h to increase basic strengths. The reaction mixture was refluxed for 10 h at 60°C. It was observed that $\text{Ca}(\text{OCH}_3)_2$ gives 98% yield among other derivatives the reason for highest yield of $\text{Ca}(\text{OCH}_3)_2$ is it had a remarkable basic strength in the range of 11.1–15.0 and these results demonstrated the reasons why $\text{Ca}(\text{OCH}_3)_2$

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Mgo	0.3	250	98	[99]
Mgo/SiO ₂	5	220	96	[125]
MgO-MgAl ₂ O ₄	10	65	57	[99]
Mgo-La ₂ O ₃	2.2	25	100	[104]
MgO-ZrO ₂	0.5	65	100	[103]
MgO/CaO	1	60	92	[105]
Mg-Al HTA	4	65	90.5	[125]
Mg/Al/Zr	1.5	70	74	[91]
Mg/Al HT	1	100	75	[91]
Mg/Al	1	130	65	[91]
MgO	1.5	75	12.1	[109]
MgO-SBA-15	5	220	96	[125]
MgO/Al ₂ O ₃	3	180	92	[108]
MgO/Al ₂ O ₃	2	65	66	[108]
MgO/Cao	1	60	92	[108]
Mgo-CaO	2	60	92	[114]
CaO	1.5	75	91.1	[109]
CaO	2	65	98	[110]
Oyster shell	4	65	96	[111]
Mud crab shell	2.5	65	98	[112]
Egg shell	2	60	90	[113]
Cao/SiO ₂	5	60	95	[114]
CaMg(CO ₃) ₂	3	60	99.9	[105]
Ca(OCH ₃) ₂	10	65	98	[115]
CaTiO ₃	10	60	79	[115]
CaMnO ₃	10	60	92	[115]
CaFe ₂ O ₅	10	60	92	[115]
CaZrO ₃	10	60	88	[115]
Ca(NO ₃) ₂ /Al ₂ O ₃	3	60	94.3	[39]
CaCeO ₃	10	60	89	[115]
SrO	0.5	65	95	[96]
Sr(NO ₃) ₂ /ZnO	5	65	96	[119]
CaO/ZnO	0.5	65	93.5	[105]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Mg–Al hydrotalcite	9	65	67	[6]
Mg–Al–CO ₃ hydrotalcite	3	180–200	99	[122]
Mg–Al hydrotalcites	4	65	90	[124]
Mg–Al hydrotalcite	6	100	96	[124]
Mg–Co–Al–La	5	200	97	[125]

Table 3. Alkaline earth metals and metalloids catalysts used for the transesterification of oils.

exhibited a greater catalytic activity than CaO and Ca(OH)₂ for others the resulting yield is from 79 – 90%. CaZrO₃ and CaO–CeO₂ exhibit high durability and it can be used in future as heterogeneous catalyst [99].

Application of strontium oxide- and nitrate-based catalyst is also reported in literature, there reported order of activity observed to be BaO > SrO > -CaO > MgO [100].

In past, the activity of MgO, CaO and SrO were are studied by different researcher for bio-diesel productions and the observed conversion efficiency of followings ranging from 90 to 95% Liu et al. reported the use of SrO for transesterification of soybean oil. It is examined that SrO gives 95% yield in just 30 mins reaction time and at 65°C temperature as reported by Liu et al.[86, 101–103].

The catalytic efficiency of activated Sr(NO₃)₂/ZnO was also examined by Yanz et al., the catalyst was prepared by using 2.5 mmol of strontium nitrate Sr(NO₃)₂/g on ZnO by wet impregnation process followed by calcination at 600°C for 5 h. Transesterification of soybean oil was carried out in batch reactor at 65°C 12:1 methanol:oil molar ratio. Under this condition, reaction was complete in 5 h by giving 96% conversion of FAME [104].

Alkali metal hydrotalcite is another group catalyst which has been used extensively for triglyceride conversion into FAME. Hydrocalcite are important as their acidic and basic properties can be monitored by fluctuating their composition and hence can be used for fatty acid methyl ester production. Helwani et al. and Zabeti reported use of hydrotalcites as catalyst for the production of biodiesel. Magnesium-based hydrotalcite are common and mostly synthesized by co-precipitation method [24, 50, 105].

Most commonly hydrocalcite has three groups of basic sites, like weak basic site(OH), medium basic site (oxygen in metal oxide) and strong basic sites (O₂ anions) present in hydrocalcite [106].

Hydrocalcite possesses large pore than the normal metal oxides, the large pro size of this hydrocalcite results in higher catalytic then normal common metal oxides. Magnesium and aluminum-based hydrocalcite have been reported in literature. Mg-based hydrocalcite showed optimum activity from 350 to 600°C calcination temperature. Xie et al. reported Mg–Al-based hydrocalcite for transesterification of plant oil. It was observed that at high calcination temperature catalyst become deactivated. The hydrocalcite calcinated at 500°C

temperature for 8 h, 67% conversion of fame ware reported at 9 h reaction time with methanol to oil ratio of 15:1. While Barakos reported 99% conversion of oil by using Mg–Al–CO₃ hydrotalcite as catalyst. He has calcinated Mg–Al–CO₃ hydrotalcite calcinated at 350°C temperature for 6 h and methanol to oil molar ratio of reaction was 6:1 at 200°C reaction for 3 h [6, 91, 107–110].

6. Biodiesel production from transition metals, lanthanide actinides and their derivatives

Transition metal oxides and chlorides are widely examined in several chemical reactions concerning their activity in plant oils transesterification. Transition metal complexes are also been studied in literature as active materials for esterification reactions. [111].

In literature, the best reported catalytic activity and strength were detected for the CaZrO₃ and CaOCeO₂ heterogenized catalysts. It is found that Zr and Ce catalyst endured highly active up to 7th, and gave up to 80% yield in methyl esters were obtained within in 60 min reaction at 60°C by using 6:1 oil to methanol ratio. Possessing of variable Lewis acidity, metal oxidation state and ion radius size makes transition metal oxides and Oxo salts more suitable for transesterification catalysts. Due to their acidic properties, a lot of transaction metals like zinc, zirconium and titanium oxide are best among the transition metal oxides which are famous and broadly used for biodiesel synthesis. Past molybdenum- and tungsten-containing solids have been accounted in various reactions in which the acidity profile assumes essential parts in isomerization, cyclic alkene oxidation, alcohol dehydration and plant oils transesterification [16, 29, 112].

There have been a few research provided details regarding the utilization of sulfated zirconia as a strong catalyst for triglyceride conversion of various oils, because of its strong acidity it was discovered that the causticity is advanced when the surface of this zirconia metal contains anions of sulfate and tungstate. Catalytic activity of SO₄²⁻/ZrO₂ was studied by Lam et al., and WO₃/ZrO₂ was studied by Sunita. It was accounted for that the specific surface area and active site number assume to be an essential part in the catalytic action.. Sulfated zirconia showed more activity in less time for conversion of oil into biodiesel than tungstated zirconia [113, 114].

Zinc(II) Schiff base complexes have been reported by martino as catalysts for biodiesel production from waste oil. He demonstrated that zinc(II) species can work in mild condition for catalyzing the triglyceride conversion of plant oil and activity could modified by a fine choice of the anions of the metals on the ancillary bidentate ligand. Homogeneous acid catalyst was widely studied in literature. Despite they have lower activity, yet strong acid catalyst have been utilized as a part of numerous modern commercial process since they contain a variety of acid sites with various quality of Bronsted or Lewis acidity. Nafion-NR50, tungstated, sulfated zirconia and zirconia possesses sufficient acid site and had been used in transesterification. Nafion were found to be the best, among these catalyst, because of their acid Nafion has hindrances of high cost and lower activity contrasted with liquid acids so it is not exceptionally practical catalyst for commercial application [115–117].

Most transition metal are expensive and heterogeneous catalyst of these metal need high temperature and pressure to achieve high conversion of oil. It was found that pure and mixed ZnO exhibits the conversion efficiency ranging from 90 to 95%. while strontium loaded at fly ash ZnO-La₂O₃ and zinc aluminate have been reported. WO₃/ZrO₂ and Sr(NO₃)₂/ZnO have been used for the canalization of plant activity of zirconium and tungsten oxide investigated by Lopez et al. had found that the calcination temperatures impact on synergist properties of catalyst, concluded that more strong catalyst could be acquired after calcination at 800°C (with the development of Bronsted acid sites centralization of 161 μmol/g). At 2.5 h reaction time at 200°C reaction temperature, the methyl ester yields within the sight of WO₃/ZrO₂/MCM-41 were 85% [38, 111, 118–120].

A variety of transition metal-based solid acids SO₄/ZrO₂-Al₂O₃, SO₄/ZrO₂, WO₃/ZrO₂, SO₄/TiO₂, and Nafion had already been tested for esterification and their catalytic efficiency for esterification and transesterification of free fatty acid and triglycerides [112, 121–126].

According to the literature, microwave heating along with barium, alumina, silica, zinc aluminate and zirconium-based catalysts are good catalyst for biodiesel production (Portnoff et al., 2005; Bournay et al; Ondrey et al., 2004). By using different approach, utilization of sulfated transition metal oxides such as SO₄/TiO₂, SO₄/ZrO₂, SO₄ 2-/SnO₂ + Fe₃O₄ and SO₄/SnO₂ is also reported in literature as a good catalyst [116]. Zhai et al. reported 90% activity of SO₄ 2-/SnO₂ + Fe₃O₄ catalyst at 60°C reaction temperature for 8 h reaction while Lam et al. reported 90% activity of SO₄ 2-/ZrO₂ catalyst 200°C in 1 h reaction time [113, 127–129]. In acid catalyzed reaction, heteropoly tungstate was found as active catalysts for pure and waste oil. Zirconia (ZrO₂), silica (SiO₂) and alumina (Al₂O₃) support could be used to produce heterogeneous HPAs. HPAs supported at Cs⁺, NH₄⁺ are also very active and useful as acid catalyst. Chai et al. who investigated the activity of Cs₂₅H₃PW₁₂O₄₀ has reported 96% conversion of FAME in 65°C reaction for 1 h [115, 116, 129–131]. In previous research, the activity of acids fall in CsHPW > 20%WO₃/ZrO₂ > 20%HPW/Al₂O₃ > 20%HPW/ZrO₂ > 20%HPW/SiO₂ order [47, 131–134].

Zirconium, hafnium and antimony-based transition metal catalyst were also being studied by researchers in past for transesterification. Porous zirconia, titania and alumina microsphere stabilized chemically, thermally and mechanically have been investigated by Clayton et al. [30]. Yan et al. tested Fe–Zn catalyst methanolysis of vegetable oil (using 1:15 molar ratio of methanol at 170°C, by using catalyst in amount of 3 wt.% showed TG conversion more than 99% within 5 h of reaction). It was assumed that the catalyst activity was endorsed due to the Lewis acid active sites of probably Zn²⁺ on the surface of catalyst [135].

Serio et al. studied solid acid vanadium phosphate catalyst for biodiesel synthesis, it was observed that the methyl ester yields reached 80% at 150°C within 60 min using 0.2 wt.% of the catalyst under and 1:1 of alcohol/oil molar ratio. However, the catalyst could be recycled after regeneration at high temperature [15].

Lee and Shiro used ZnO–La₂O₃, which combines acid (ZnO) and base sites (La₂O₃) for transesterification of oil they got high conversion of 96% TG in 180 min. Yan et al. used calcium oxides modified with lanthanum (La₃O₃/CaO) and observed that this catalyst is particularly

effective for transesterification at 65°C and attain a remarkable yield exceeded 94.1% at a reaction time of 1 h [136, 137]. Summary of biodiesel production from transition metals, lanthanide actinides is given in **Table 4**.

Thitsartarn et al. examined the use of CeO₂-CaO mixed oxides as catalysts for biodiesel production. They had studied several reaction parameters carried out at optimal transesterification. They concluded that CeO₂-CaO mixed oxides gives best catalytic activity at 85°C in 2 h with 97% yield [138].

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
ZnO/CaO	1	60	94.2	[105]
ZnO-Al ₂ O ₃	0.5	200	99	[153, 154]
ZrO ₂	1	200	64.5	[131]
SO ₄ 2-/ZrO ₂	1	200	90	[128]
SO ₄ 2-/TiO ₂	1	20	40	[127]
SO ₄ 2-/SnO ₂	3	180	65	[155]
SO ₄ 2-/SnO ₂ +Fe ₃ O ₄	8	60	90	[142]
SO ₄ 2-/SnO ₂ +Al ₂ O ₃	3	180	80	[128]
SO ₄ 2-/ZrO ₂ -TiO ₂ /La ³⁺	5	60	95	[128, 156]
ZrO ₂ /Al ₂ O ₃	Continuous run	250	97	[81]
WO ₃ /ZrO ₂	5	200	97	[129]
TiO ₂ /ZrO ₂	Continuous run	250	95	[16]
MnCex	5	140	87	[157]
WO ₃ /ZrO ₂ /Al ₂ O ₃	Continuous run	200	90	[158]
WO ₃ /ZrO ₂ /MCM-41	2.5	200	85	[159]
H3PW12O ₄₀ /ZrO ₂	10	200	77	[130]
H3PW12O ₄₀ /Ta ₂ O ₅	24	65	65	[160]
Cs ₂₅ H ₃ PW ₁₂ O ₄₀	1	65	96	[131]
MnO-TiO	0.35	260	92	[161]
Fe-Zn	5h	170	99	[150]
CaMnO ₃	10	60	75	[75]
Al ₂ O ₃ /PO ₄ 3-	5	200	69	[162]
Al ₂ O ₃ /ZrO ₂ /WO ₃	20	75	85	[163]
VOPO ₄ ·2H ₂ O	1	150	80	[15]
La ₃ O ₃ /CaO	1	60	94.3	[126]
CeO ₂ -Cao	2	85	97	[164]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
La ₂ O ₃	2	200	97.5	[165]
Eu ₂ O ₃ /Al ₂ O ₃	8	70	63.2	[166]
Sulphonated carbon	2.5	260	90	[167, 168]
Sulphonic/SiO ₂	5	150	60	[169]
Sulphonic acid/SBA-15	8	180	96	[170]

Table 4. Transition metals, lanthanide actinides based catalysts used for the transesterification of oils.

Bancquart et al. investigated the activity of La₂O₃ for glycerol transesterification to investigate the relationship between activity and basicity. It was reported that at high temperature of 200°C, the same yield was 97.5% in 2 h. On the other hand, both these metals are very expensive and not economical for the production of biodiesel [139].

Li et al. studied the activity of a novel solid super base of Eu₂O₃/Al₂O₃ complex for transesterification triglycerides with alcohols, he observed 63.2% yield of FAME in 8 h reaction at 195°C [140].

Currently, due to the believe that solid base catalyst are more environmental friendly and could replace acid catalyst, researches are focusing at the synthesis of novel, stable and economical solid acid catalysts for transesterification reaction [68].

7. Bio catalyst

The utilization of lipases (triacylglycerol acyl hydrolases) as biocatalyst for the production of biodiesel has become more appealing since the ease of glycerol recovery (byproduct) and purification of FAME [141]. Plethora of research reports demonstrated the used of lipase as a catalyst for production of biodiesel; however, this technology has not received much commercial attention due to the high cost of enzyme [141]. To overcome the drawback of free lipases, recent research efforts have been made toward the immobilization of lipases on solid support (such as zeolite, Celite, silica gel, inorganic nanoparticles, acrylic resin and textile membrane etc.) which not only reduce the cost in terms of reusability but also increases the number of available active sites [142]. Crosslinking, covalent bonding, adsorption and entrapment are the most common approaches that are involved in immobilization of lipase onto the solid support [143–145].

Casimir et al. stated that enzymes can be used as biocatalyst for transesterification reaction, for example, *Candida antarctica* lipase many enzyme like *Pseudomonas fluorescens* Rhizomucor miehei and *Chromobacterium viscosum* [146] and *Rhizopus oryzae* lipase [147] have been used as enzyme catalyzed transesterification reactions. Immobilized lipase have been used by Tan et al. for biodiesel synthesis covalent bonding, crosslinking, encapsulation, entrapment and adsorption have also being reported in literature to rise the stability of lipase in FAME synthesis.

It was investigated that recombinant DNA technology can be used to produce large quantities of lipases. Casimir et al. recommended that the utilization of immobilized lipase may diminish the general cost of biodiesel production and lower downstream preparing issues and this is ecologically suitable with respect to other conventional methods. Watanab et al. built up a three-advance methanolysis process for biodiesel synthesis by utilizing *Candida antarctica* lipase for persistent generation of biodiesel fuel from vegetable oil. It was observed that 95% yield can be gotten by utilizing 4% immobilized *Candida* lipase as a catalyst at 308°C reaction time in a 20-or 50-ml screw-topped vessel with The 1:2 molar amount of methanol against the aggregate unsaturated fats. Hideki et al. additionally reviewed utilization of enzymatic-catalyzed transesterification to reduce problems associated with homogeneous catalysis. The author revealed the use of immobilized *antarctica* lipase (Novozym-435) for high FFAs feed stock for biodiesel production [147].

Additionally, Shah et al. used lipase for synthesis of biodiesel from *jatropha* oil. He used solvent-free system for screening of pancreas porcine, *Candida rugosa* and *Chromobacterium viscosum* for the production of biodiesel. 0.5 g of *jatropha* seed oil in a vessel having 1:4 molar ratio of ethanol and 50 mg of enzyme was introduced and incubated at 40°C with constant stirring at 200 rpm. They observed 62–71% yield of ester by free-tuned enzyme of lipase (*Chromobacterium viscosum*) in a process time of 8 h at 40°C.

8. Conclusion

The generation and utilization of biodiesel have seen a quantum bounce in the current century because of advantages related to its capacity to relieve ozone depleting substance (GHG). There is a huge number of non-edible plants oil use for biodiesel synthesis through transesterification of fats, a stable catalysts in terms of, catalytic life, recyclability and lower cost are critical as these directly affect the general cost of the overall process. The different choices of heterogeneous strong catalysis were accounted for the particular research results of transesterification on heterogeneous catalysis majorly centered on examining the suitable oil source, methanol to oil molar proportion, and assessing the accessibility of catalyst. Unlike homogeneous, heterogeneous catalyst are cost effective and environmental friendly can easily be reused and recovered.

As lower reaction rate and side reactions make the use of catalyst limited, solid acidic catalysts for biodiesel synthesis. Solid acid catalyst are very useful in term or their ability to work in one step and are able to convert oils with high amount of free fatty acids (FFA) into biodiesel.

Presence of water in feedstock obstructed the activity of the basic heterogeneous catalyst. Be that as it may, strong base work quicker and gives higher TG conversion than an acid catalyst. Amendment of the catalyst by monitoring different aspects makes catalyst more suitable for transesterification and makes it more energy intensive. Mutual esterification and transesterification could be simultaneously done by using acid-base catalysts. On the other hand enzymatic catalysts are highly promising but enzymes carried out transesterification reaction in very slow rate. On the other hand heterogeneous catalyst work smoothly when reaction temperature, pressure and molar ratio of alcohol to oil is considerably high.

Efficiency of catalyst also depends upon calcination time and temperature. Calcination leads to alteration of the starting reactant into new compound possessing high catalytic activity than original compound. It is because calcination increases basicity, pore size and pore volume specific surface area and active site concentration could at catalyst.

Only few researches specify the industrial level production of FAME by implementing the heterogeneous catalyst method. In past, a lot of researches were done to explore and exploit synthesis and use of novel heterogeneous catalysts in the production of FAME. Some of the reasons for the recent growth and development of heterogeneous catalysts include among others are biodiesel yield of 98 wt% and simplicity in catalyst separation process, high-purity byproducts, less cost of separation and low energy.

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