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REVIEW ARTICLE

Biodiesel Production through Heterogeneous Catalysis Route: A Review

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Depletion of oil reserves, increasing prices of petroleum products, and environmental concerns related to air pollution are the main driving forces for utilizing renewable energy resources to replace fossil fuels. Vegetable oils can be used to produce biodiesel. Biodiesel is obtained by transesterification of vegetable oil with alcohol using homogeneous or heterogeneous catalysts. Commercial homogeneous catalysts in the biodiesel production industry are facing challenges such as separation difficulties and severe corrosion which will lead to the increment of production and maintenance cost. Herein, this paper focuses on the comprehensive review of literature reported on the usage of heterogeneous catalyst used in biodiesel production. Compared to other commercial catalysts, the usage of heterogeneous catalyst possesses several advantages such as abundantly available, cheaper raw materials, reusable, non-toxic and biodegradable. Carbon material synthesized from biomass which acts as the efficient support for active sites due to its high porosity and surface area characteristic has been studied widely.

Keywords: Biodiesel, heterogeneous catalysts, metal oxides, renewable energy, transesterification

Introduction

High energy demand, shortage of fossil fuels, and environmental issues encourage the search for bio-based petroleum derivatives. Biodiesel is considered as alternative and has caught a lot of attention due to its renewable nature, eco-friendliness, and prospective toward decreasing deplete productions.[1,2] Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from nontoxic, biological resources such as vegetable oils,[3,4] animal fats,[5,6] or even used cooking oils (UCO) [7,8] and other food waste.[9] India is importing more than 80 % of its fuel demand and spending a huge amount of foreign currency on fuel. Biodiesel is gaining more and more importance as an attractive fuel due to the depleting nature of fossil fuel resources. The purpose of transesterification process is to lower the viscosity of the oil. The main drawback of vegetable oil is their high viscosity and low volatility, which causes poor combustion in diesel engines. The transesterification

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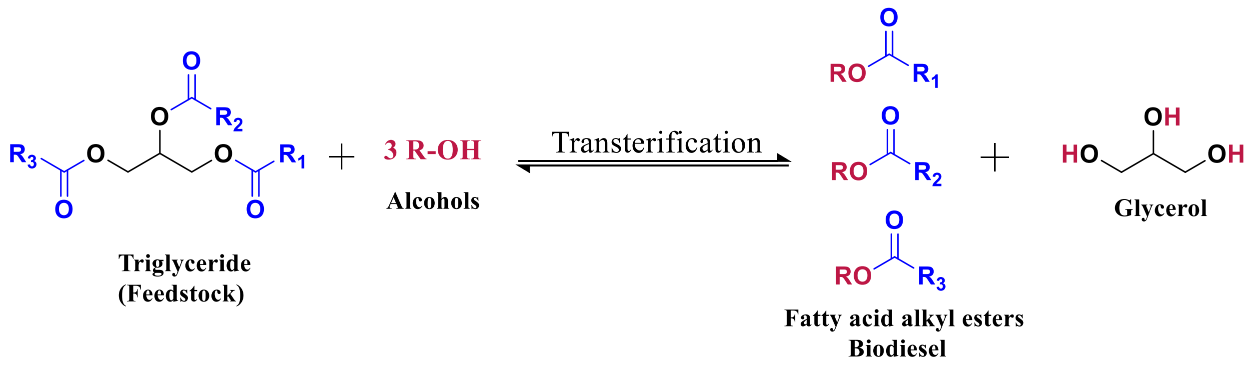
is the process of removing the glycerides and combining oil esters of vegetable oil with alcohol. This process reduces the viscosity to a value comparable to that of diesel and hence improves combustion. Biodiesel emits fewer pollutants over the whole range of air–fuel ratio when compared to diesel.[10]

FAME (biodiesel) is prepared from renewable feedstock, i.e., edible and non-edible vegetable oils as well as animal fats. It is obtained by a catalyzed reaction of the triglycerides (TGs) in the vegetable oils or animal fats with a monohydric alcohol. Oils and fats are basically a mixture of lipids; ~95% are triacylglycerols, diacylglycerols, monoacylglycerols, FFA, and sometimes phospholipids or other types of minor compounds. NaOH or KOH-catalyzed transesterification of TGs is conducted under atmospheric pressure and temperatures around 60–70°C with methanol. After completion of the experiment the reaction mixture is allowed to settle. The lower layer is glycerol (GL)-rich while the upper layer consists mostly of methyl esters (ME). The ME collected from the upper layer is washed with water to remove impurities for further processing. Unreacted methanol is collected by fractional distillation and sent to a rectifying column for decontamination and reprocessing.[11]

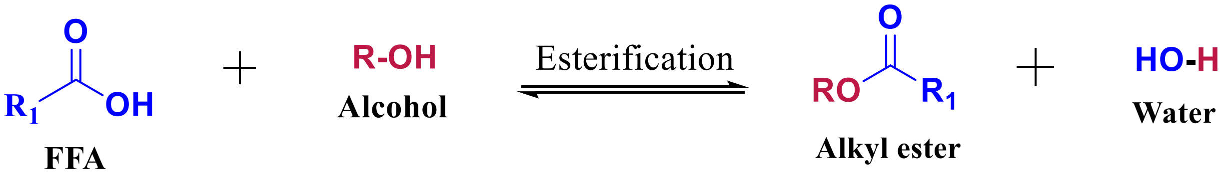
Researchers and scientists had developed different methods for biodiesel production from different bio fuels. A brief review of these methods has presented here. Most of the researchers/ scientists reported that the production of biodiesel was more when the process was used a catalyst. Ramadhas *et al.*[12] studied biodiesel production from high free fatty acid rubber seed oil. They developed a two-step transesterification process to convert the high free fatty acid oils to its mono-esters. Waste frying oils transesterification was studied by Tan *et al.*[7] with the purpose of achieving the best conditions for biodiesel production. Laskar *et al.*[13] produced biodiesel from jatropha curcas oil using a heterogeneous solid mesoporous, acid-functionalized polymeric catalyst.

Simultaneous esterification and transesterification reaction

Transesterification reaction is used for biodiesel is production. In the presence of a catalyst, transesterification of TG and alcohol, typically methanol, yields fatty acid alkyl esters (biodiesel) and GL. In a process similar to hydrolysis, transesterification, also known as alcoholysis, is the disarticulation of alcohol from an ester by a separate alcohol. This method has been widely used to reduce the viscosity of TGs. Methanolysis (Scheme 1) occurs when methanol is utilized as a solvent in the aforementioned transesterification reaction.[14] Three moles of alcohol and one mole of triacylglyceride are required to create ME, with GL as a by-product, according to the stoichiometry of the reaction. Because transesterification is a reversible reaction, at least 1.6 times more alcohol is required for the entire reaction. Because of their lower prices and better reactivity, CH_3OH and $NaOCH_3$ are commonly used in industrial-scale biodiesel manufacturing. However, as illustrated in Scheme 2, the esterification reaction, which is a reaction between carboxylic acids and alcohols to produce esters, is required to convert all free fatty acids (FFA) in vegetable oil into biodiesel.[15] Typically, these transesterification and esterification procedures are carried out in two pots. Typically, the high FFA content of vegetable oil is transformed to esters (FAME) using an acid catalyst-assisted esterification reaction, followed by a basic catalyst-assisted transesterification reaction to convert triglycerides to FAME. To reduce the time and expense of biodiesel production, simultaneous transesterification and esterification in one pot are very desirable for converting both triglycerides and FFA of vegetable oil (with high FFAs) to FAME.



Scheme 1: Transesterification of TGs of vegetable oil to biodiesel



Scheme 2: Esterification of FFA content of vegetable oil to biodiesel.

Feedstocks for biodiesel production

About 34% of edible oil is estimated for biodiesel production and it will be increased in future. Waste cooking oil and non-edible oils in biodiesel production could be alternative sources.[16]

Biodiesel has been mainly produced from edible vegetable oils all over the world. Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry.[17] However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long term.[18]

Different countries use various feedstocks based on their local availability. These include traditional sources like edible oils, non-edible sources, and other sources like waste cooking oils or animal fat.[19] The most commonly used edible oils are sunflower oil, soybean oil, rapeseed oil, peanut oil, olive oil, canola oil, palm oil, coconut oil. Non-edible sources include jatropha oil, stillingia oil (Chinese tallow seed oil), karanja (*Pongamia pinnata*) oil, neem oil, castor oil, linseed oil, and rubber seed oil. Waste and other feedstocks include mutton fat, algae oil, waste cooking oil, microbial oils, waste fish oil, micro algae.

Types of heterogeneous catalyst

Transesterification reactions can be catalyzed by alkali, acid, or enzyme. Enzymatic transesterification is thought to be the most efficient way for producing biodiesel.[20,21] However, the cost of the catalyst is quite high, and the reaction rate is too slow, limiting its use.[22]

Today, homogeneous base catalysts are the most popular choice for production of biodiesel in an industrial scale.[23] However, the presence of free fatty acids (FFA) and water makes the homogeneous base catalyst reaction extremely sensitive. Furthermore, the production of soaps as a result of the side reactions of neutralization and saponification would obstruct the separation and purification process, result in a high volume of wastewater, and add to the operating costs. Because of this condition, this catalyst is harmful to the environment.[24] Furthermore, the catalyst recovery and regeneration are difficult, impractical, necessitate additional processing steps, and are extremely expensive.[25]

The use of heterogeneous or solid catalysts in biodiesel production has sparked an interest. The catalysts are neither consumed nor dissolved in the reaction mixture, making separation of the product easier after. Furthermore, the recovered catalyst can be re-used in the reaction, reducing catalyst consumption and extra expenses.[26] The heterogeneous-based process has several advantages, including noncorrosiveness, ease of separation, and longer catalyst life.[24,27] Moreover, Sani *et al.*[25] stated that mass transfer efficiency is limited within a bulky molecule hence resulted in the poor conversion into biodiesel. Additional problems faced by solid catalyst are a low number of active sites, micro porosity, leaching, toxic, expensive, derived from non-renewable resources and environmentally unfriendly.[28,29] Hence, in order to produce an excellent solid acid catalyst, the catalyst must comprise of more specific surface area (hydrophobicity, external catalytic sites, etc.) and a large pore diameter.[30]

Heterogenous catalysts used for transesterification of oil to biodiesel are mainly divided in two classes: (1) solid base catalyst and (2) solid acid catalyst which are discussed below:

1. Solid base catalysts

Basic heterogeneous solid catalysts have received the most attention in the last few years because they can overcome the limitations of homogeneous basic catalysts, it also has good catalytic activity under mild reaction conditions. Most catalysts, on the other hand, are only effective with biodiesel feedstocks that contain less FFA; eventually, the catalysts will react with the FFA and produce soap through the saponification process making separating biodiesel from glycerol time-consuming, lowering biodiesel yield. Metal oxides, mixed metal oxides, and other solid base catalysts have been described in the literature, are thoroughly discussed in this section.

Metal oxide

As a potential substitute to the homogeneous base catalyst, Table 1 shows various metal oxides such as, SrO, CaO, Co(II)@chitosan, MgO, SO_4^{-2}/ZrO_2

and BaO, which are known to be outstanding heterogeneous catalysts due to their ease of availability, low cost, superior activity, and selectivity.[31] Because transesterification requires mild reaction conditions, CaO as a catalyst becomes more desirable. While the reaction conditions were modified, Kouzu *et al.*[32] discovered a high FAME yield of 95% when transesterifying soybean oil with the CaO catalyst. According to Granados *et al.*[33] CaO calcined at 700°C showed very considerable activity in the synthesis of biodiesel from sunflower oil, providing 94% biodiesel.

Using a sea sand-derived catalyst, used cooking oil and refined oil as a starting material were studied for transesterification by Muciñoet *et al.*[34]. $CaCO_3$ is abundant in sea sand, to synthesis CaO sea sand become good source by thermal treatment after 2h at 800°C it converted to calcium oxide. CaO produced has a lot of basic active sites, which means it has a lot of catalytic activity. However, a 12:1 MTOR give show the ease of product separation and washing. Using safflower oil, soybean oil, and cooking oil, under the optimized conditions 96.6%, 97.5% and 95.4% FAME yield were achieved respectively at reaction time of 6 hand 7.5% catalyst loading.

In the meantime, Piker *et al.*[35] studied egg shells and were tested as an active catalyst for biodiesel generation utilizing waste cooking oil (WCO) at room temperature. Without any pre-esterification treatment, continuous stirring for 11 h with a 5.8 w.% catalyst and 6:1 MTOR resulted in a FAME yield of 97%. According to the findings, the catalyst may be reused 10 times with new soybean oil and 5 times with waste cooking oil. After three months of storage, the catalyst performed well however, one year of storage resulted in a 10 % reduction in FAME product.

Bazargan *et al.*[36] studied CaO catalyst using thermal gasifier from palm shell kernels (PSK). With sunflower oil and methanol, it was used for transesterification. Palm kernel shells produced enormous amounts of ash as a result of the power system's energy input and heat, resulting in palm kernel shells biochar (CKSB). CaO was discovered to have more active sites than calcined PSKB, which could be due to its higher purity and bigger surface area. The size of the PKSB material was revealed by SEM to be in the range of 1 to >100 mm.

In another work, Rezaei *et al.*[31] investigate the discarded mussel shell as a source of calcium carbonate that converts to calcium oxide catalyst at temperatures above 950°C during calcination. At 60°C the transesterification reaction was performed with methanol, soybean oil and mussel shell catalyst. Response surface methodology (RSM) was used to investigate the reaction. The optimum catalyst synthesis reaction conditions were determined to be a calcination temperature of 1050°C and a catalyst loading of 12 wt.%. Under the optimized conditions 94.1% pure biodiesel was obtained. In five recycle experiments, the catalyst that was not calcined between cycles and had better performance than the catalyst that was calcined at 1050°C. This could be due to re-calcination resulting in a smaller surface area.

Furthermore, Nualpaeng *et al.*[37] investigated CaO -based catalysts generated by gel-combustion method for biodiesel generation utilizing palm oil as the starting material. The catalyst exhibited fine crystalline and also had a high basicity, total pore volume and specific surface area when compared to samples obtained using the direct calcination technique. Using optimum conditions of a 10% catalyst, 18:1 MTOR and reaction temperature 60°C under steady stirring at 600 rpm, 97.1 wt. % yield of biodiesel was observed in 90 minutes reaction time. Following four repeated cycles with no post-treatment of the catalyst, the catalyst was also reusable with consistent FAME production.

In supercritical/subcritical temperatures, Wang and Yang38 found that the activity of the catalyst was increased by Nano-MgO. With a stirring speed of 1000 rpm and 3 wt.%. Under 36:1 MTOR, 28.7 MPa reaction pressure and reaction temperature 533K, within 10 minutes the transesterification reaction was substantially completed more than 99% yield. The greater reaction rate with nano-MgO was largely due to higher stirring and the lower activation energy (75.94 kJ/mol).

In this line, Mootabadi *et al.*[39] reported biodiesel production using ultrasonic-assisted from palm oil with metal oxides BaO. Activity of the catalyst in the production of biodiesel using ultrasonic-assisted was compared to that of the conventional magnetic stirring process, and found that in 60 min the ultrasonic process produced 95.2% biodiesel yield using BaO, whereas the traditional stirring process took 3–4 h. The results of the study explore the importance of ultrasonication in chemical processing, especially in production of biodiesel. Furthermore, the influence of ultrasonic amplitude on palm oil biodiesel production was investigated, and it was shown that a 50% ultrasonic amplitude produced the best biodiesel.

According to Jitputti *et al.*[40] biodiesel production using crude coconut oil and crude palm kernel oil was examined using SO_4^{-2}/ZrO_2, ZrO_2, KNO_3/KL zeolite, ZnO, KNO_3/ZrO_2 and SO_4^{-2}/SnO_2, and found that for both oils, the catalyst SO_4^{-2}/ZrO_2 had the maximum reactivity, providing biodiesel yields of 86.30% and 90.30%, respectively.

da Silva *et al.*[41] reported on biodiesel production using soybean oil from Cu(II) and Co(II) impregnated chitosan catalysts. Cu (II) adsorption on chitosan is superior to Co adsorption (II). However, using the optimal reaction conditions, Co (II) @chitosan produced a higher biodiesel yield (94.01 %) than Cu (II)@chitosan (88.82%).

In another paper, Liu *et al.*[42] described the SrO^-

catalyzed transesterification of soybean oil. At 70°C and 30 minutes, the catalyst demonstrated outstanding activity with a high yield of 95%. The catalyst is extremely stable and can be reused for up to 10 times.

Overall, metal oxides are very reactive and thermally very stable base catalysts for biodiesel and showed good recyclability. The basicity test by Hammet titration revealed a high basicity of catalyst, in the region 9<H_<15. In the meantime, leaching of metal oxides is a major concern during biodiesel synthesis, hence reduced the reusability of the catalyst. Therefore, a means to reduce the leaching by modification of metal oxides in an interesting research field at present.

Mixed metal oxide

Mixed metal oxides have a lot of interesting features, particularly if one component is different from the others. Compared to single metal oxides, mixed metal-oxide catalysts are considered to have higher acidic,[43] basic strength,[44,45] stability,[46] and surface area.[45] As a result, a variety of highly reusable, efficient, and stable solid catalysts were developed. A mixture of two metal oxides, for example, can display acid–base characteristics or other unique aspects despite their separate qualities.[47] High-reactivity mixed metal oxides can also be generated at much lower temperatures, which makes them very useful in catalysis. Various mixed metal oxide catalyst are shown in Table 2.

Using an impregnation approach, the transesterification of JCO with methanol was investigated using K_2CO_3, K_2SiO_3, and KAc supported on mesoporous silicas (SBA-15 and AlSBA-15). Al doping in AlSBA-15 helped to produce weak and medium acid sites, which helped to weaken the dissolution of Si atoms caused by degradation of the K_2SiO_3 base while retaining the pore structure of AlSBA-15, so improving the stability of AlSBA-15 support. Because of its higher basicity, the K_2SiO_3 impregnated AlSBA-15 catalyst produced somewhat more biodiesel than the K_2CO_3 and KAc impregnated catalysts. After calcination, the K_2SiO_3/AlSBA-15 had the highest basicity, which could be owing to a greater contact between the K_2SiO_3 active components and the AlSBA-15 silica. In terms of activity, K_2SiO_3-impregnated catalysts beat K_2CO and KAc-impregnated catalysts. Using a K_2SiO_3/AlSBA-15 catalyst with 30 wt. % K_2SiO_3 loading on AlSBA-15 support calcined at 600°C, a 9 :1 MeOH:JCO molar

Table 1. Various metal oxide catalysts reported for biodiesel production

Sl. No.	Catalyst	Feedstocks	Condition[a]	Conversion (%) / Yield (%)	Ref.
1	CaO	Soybean oil	24 : 1, 12, 60, 8	94.1(Y)	31
2	CaO	Soybean oil	12 : 1, 8, 65, 3	95 (Y)	32
3	CaO	WCO	12 : 1, 7.5, 60, 6	95.4 (Y)	34
4	CaO	WCO	6 : 1, 5.8, RT, 11	97 (Y)	35
5	CaO	Sunflower oil	9 : 1, 5, 60, 5	NP	36
6	CaO	Palm oil	18 : 1, 10, 60, 1.5	97.1 (Y)	37
7	MgO	Soybean oil	36 : 1, 3, 260, 10 (mins)	99 (Y)	38
8	BaO	Palm Oil	9 : 1, 3, 65, 1	95.2 (Y)	39
9	SO_4^{2-}/ZrO_2	Crude coconut oil	6 : 1, 3, 200, 1	86.30 (Y)	40
10	Co(II)@chitosan	Soybean oil	1 : 5, 2, 70, 3	94.01 (C)	41
11	SrO	Soybean oil	6 : 1, 3, 70, 30 (mins)	95 (Y)	42

[a] MTOR, catalyst loading (wt. %), temperature (°C), time (h).

ratio, 2.5 h, 60°C, , and a 3% catalyst loading, FAME conversion of more than 95% was achieved. The catalytic activity decreased slightly when it was reused, owing to the leaching of some potassium species and the adsorption of organic deposits on the catalyst.[46]

Sun *et al.*[44] also investigated the production of biodiesel using a La_2O_3-loaded ZrO_2 catalyst with a La_2O_3 content ranging from 7 to 28 wt. %. The sunflower oil and FAME conversion were basically related to the basic property of La_2O_3/ZrO_2 catalyst, the basic property of loaded La_2O_3 was affected by the cooperation of support ZrO_2 and surface La_2O_3. The maximum biodiesel production 84.9% using sunflower oil was achieved using the optimized catalyst (21 wt. % La_2O_3 loading on ZrO_2 and calcination at 600°C).

The basic catalyst sodium zirconate (Na_2ZrO_3) was used to carry out the transesterification reaction of soybean oil. Under a solid-state reaction of ZrO_2 and Na_2CO_3, Na_2ZrO_3 was formed. Because of its basic strength and stability during the transesterification reactions, the analysis shows that Na_2ZrO_3 had high catalytic activity, 98.3% conversion was achieved under ideal reaction conditions of reaction temperature 65°C, 3 wt. % catalyst and 3 h reaction time. FAME conversion decreased as the cycle progressed as confirmed from XRD, which could be due to catalyst loss during solvent evaporation or particle surface inactivation.[48]

In the meantime, Lee *et al.*[45] studied various quantities of Mg to Zn, MgO-ZnO mixed metal oxides catalyst for biodiesel production. The physiochemical properties of MgO-ZnO mixed metal oxides were superior to those of ordinary MgO and ZnO oxides. The physicochemical properties of the MgO-ZnO catalyst outperformed those of ordinary MgO and ZnO bulk oxides. Because of the presence of the MgO phase, the Mg/Zn catalyst surface area increased as the atomic ratio grew from 0.5 to 10.0 Furthermore, utilising CO2-temperature-programmed desorption, the number of basic sites on the magnesium-based mixed oxide was larger than that of both MgO and ZnO with substantial basic strength (CO_2-TPD). The synergy effect of the Mg$^-$ Zn binary oxide was due to the interactions between Mg and Zn. By coprecipitation with various Mg/Zn atomic ratios the catalysts were formed and then calcined for 6 h at 800°C. The atomic ratio of Mg/Zn of 8 (MZ8) was chosen as the best catalyst for the reaction. At a 25:1 MTOR, 120°C reaction temperature, catalyst loading of 3 wt. % and a reaction time 3h, MZ8 gave 83 % yield. The reusability of catalyst revealed that the catalyst weakens over the course of the 5 runs due to slight leaching of the active component during the reaction, which was confirmed by atomic absorption spectroscopy (AAS) analysis.

Mutreja *et al.*[49] discovered that a catalyst with a 1 : 3 La/Mg atomic ratio produced much higher FAME conversion 96% in just 20 mins at 65°C. The impregnation of K species could aid in the formation of greater basic strength and larger catalytic site, moreover, enrichment of Mg in the catalysts resulted in increase in average particle size and crystal lattice distortion, the catalysts were found to be the best choice because they use less expensive Mg in bulk, have fewer K species, and have good catalytic activity. The reusability of the catalyst was checked and after third cycle biodiesel conversion 87% was obtained, the declined in FAME conversion is due to leaching of K+ which was found to be 4.5 ± 0.2 ppm.

Furthermore, Wen *et al.*50 obtained the TiO_2–MgO catalyst using the sol–gel method, and it was used for biodiesel production from WCO. Because of the defects caused by the substitution of Ti ions for Mg ions in the magnesia lattice, titanium improved the catalyst's stability. In the manufacture of FAME, the catalyst with a 1: 1 Ti to Mg molar ratio and calcined at 923 K was determined to be the most effective. When the catalyst MT-1-923 was utilised in the appropriate reaction conditions, a biodiesel production of 92.3 % was observed. The reusability of the catalyst after four cycle showed 81.2 % yield, the decreased in biodiesel yield was due to leaching of both metal Mg and Ti in FAME phase. This was confirmed by investigating using inductively coupled plasma atomic emission spectroscopy (ICP -AES).

Kawashima *et al.*[51] studied the FAME production from rapeseed oil using various calcium-containing catalysts ($CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and CaO–CeO_2). Under the optimised reaction conditions, CaO–CeO_2 showed excellent results around 90% conversion and high stability compared to the other calcium-containing heterogeneous catalysts. The reason of high activity of CaO–CeO_2 seems that CaO would be supported on CeO_2 and stabilized on the catalyst surface and basic sites are able to have higher contact probability of reaction substance than others. Furthermore, the strength of the affinity or solubility with highly polar materials such as glycerin might have also a large effect on the catalytic activity. The catalyst can be reused seven times with a conversion of more than 80% each time.

In another work, Chen *et al.*[52] synthesised SrO/ SiO_2 catalyst and compared its catalytic activity to that of naked SrO in the transesterification of olive oil. Although the naked SrO showed excellent catalytic activity and provided an 82% biodiesel conversion in just 15 mins, the biodiesel conversion dropped to 68.9% after 3 hrs. They claimed that a reverse reaction between FAME and glycerol was to blame for the unusual drop in biodiesel yield, proving that the catalyst not only catalysed the forward reaction but also the reverse reaction. The addition of SiO_2 to SrO, on the other hand, resulted in high activity and stability. They found that at 65°C, using SrO/SiO_2 in a 10 : 1 MTOR, they were able to achieve around 95% conversion. Furthermore, after lowering the reaction temperature to 45°C 76.9% FAME conversion was obtained. As a result, SrO/SiO_2 had a better tolerance for the water content and FFA of biodiesel feedstocks, and had a good reactivity towards transesterification of olive oil.

Previously, Veiga *et al.*[53] studied mixed oxides of Zn and Al as catalysts for the transesterification of soybean oil with methanol and found that they were effective for biodiesel production. The Zn content had a significant impact on the textural characteristics, density of basic sites, and strength distribution, according to physiochemical analysis. The density of the basic sites was determined by CO_2-TPD could be related to the catalytic nature of Zn-Al mixed oxides. Under the optimized condition 86% biodiesel conversion was obtained, there is a slight decreased in FAME conversion. The biodiesel yield, however, remained constant at 70% after the third run. Adsorption of reactants or products on the catalytic sites may have contributed to the decrease in FAME yield.

Kesic *et al.*[54] investigated CaO–ZnO mixed oxide catalysts and discovered that they are effective for biodiesel production from sunflower oil. Biodiesel conversion >90 % was obtained in the optimised reaction conditions of 3 wt. % catalyst loading, reaction time 45 mins, temperature 60°C and a 12 : 1 MTOR. It was observed that the presence of zinc increased the catalyst's resistance to CO_2 and H_2O in the air, as well as its ability to tolerate a certain amount of free fatty acids (FFAs) in the raw materials oil. CaO was shown to be stabilised by filling the mesoporous network of ZnO, preventing the active phase in the reaction from leaching.

In recent years numerous nano-catalyst have been reported in biodiesel synthesis owing to their high activity due to their high surface area compare to the bulk.[55-57] Madhuvilakku *et al.*[58] reported a TiO_2–ZnO nanocatalyst for the production of FAME using palm oil. The stability and the reactivity of the synthesized catalysts were advanced by the arrangement of deformities on the catalyst surface as a result of the substitution of Ti on the Zn grid. Under the optimized reaction conditions, they were able to obtain a 92 % biodiesel production.

According to Lu *et al.*[59] used a PDMS-PEO comb-like copolymer as a templating agent to make MgO-Li_2O catalysts. The MgO-Li_2O catalysts have a bimodal pore allocation and a 3-D interconnected very porous structure that facilitates the transesterification reaction. The catalyst has a peculiar shape of hybrid MgO and Mg_2SiO_4 crystals packed within the surface of the Li_2O nanoparticles due to Li exosolution. Since the oxygen partial negative charge of Li_2O is larger than that of MgO, scattered Li_2O nanoparticles resulted in an increase in strong basic sites. The catalyst with a Li/Mg molar ratio of 0.12 and a calcining temperature of 873K was the best and achieved biodiesel conversion 96.2%. The catalyst contained a large number of strong basic sites, which improved catalytic activity, and its anti-leaching ability was comparable to that of other catalysts. After treatment, the catalyst was recovered and reused. When the process was repeated five times, the biodiesel conversion decline to 81.2%, owing to surface poisoning, pour filling and leaching. To investigate leaching the FAME was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Su *et al.*[60] continue in this vein. Through a one-pot EISA approach, a variety of super-microporous magnesia-zirconia with various Mg/Zr molar ratios were synthesized and used as excellent heterogeneous catalysts in biodiesel production. The materials had a large amount of specific surface area. MgO not only acted as the basic sites in this process, but it was also integrated into the ZrO_2 lattice to form the solid solution that stabilized the tetragonal phase. When compared to pure zirconia (0-MgZrO) and 0.5-MgZrO-400, the addition of magnesium species increases the BET surface area significantly, resulting in 128 m2g-1 and 235 m2g-1, respectively. Zirconia has almost no activity, and the activity of ZrO_2 can also be improved by combining with MgO. The 0.5-MgZrO -400 sample has a remarkably higher activity, this can be due to the 0.5-MgZrO's high surface area and strong basicity which was later confirmed by CO_2-TPD. The 99% biodiesel conversion findings revealed that magnesia-zirconia materials had improved catalytic activity in the transesterification of soybean oil and methanol.

Furthermore, Rashtizadeh *et al.*[61] used a sol–gel method and calcination at 900°C to prepare a basic mixed-oxide-based nanocomposite of $Sr_3Al_2O_6$ that was used as a basic heterogeneous catalyst for biodiesel production via transesterification of soybean oil by methanol. The extremely basic $Sr_3Al_2O_6$ is more active in production of biodiesel than calcium and magnesium-containing catalysts due to the presence of Sr. In comparison to the CaO/Al_2O_3 catalyst, which has a basicity of 194 lmol/g CO_2 and has yielded 94% biodiesel, from CO_2-TPD studies, $Sr_3Al_2O_6$ has a basicity of 1615 lmol/g CO_2. The response surface methodology (RSM) was used to find the optimum reaction conditions, which resulted in a maximum biodiesel conversion of 95.7 0.5 %. A minor drop in catalyst activity was detected in the fourth cycle using TEM-EDS analysis, and showing that the $Sr_3Al_2O_6$ catalyst's good stability and efficiency.

Generally, mixed metal oxide are more stable and reactive compared to single metals. The synergistic effect allowed them to have better surface area, high basicity and acidity which introduce them as a great potential for catalyst in a biodiesel production. The methanol-to-oil molar ratio, concentration of the catalyst, stirring speed and reaction temperature, were found to be particular for distinct catalysts in order to achieve maximal biodiesel yield and conversion of the corresponding oil. For repeated cycles, the majority of the basic mixed metal oxide catalysts performed well. However, leaching is the main drawback which decreases the activities of the catalysts in several runs. So synthesizing leaching free mixed metal oxide is one of the most challenging work in future.

2. Solid acid catalyst

Transesterification and esterification reactions can be catalysed by acids without the formation of soap.[62] As a result, unlike base catalysts, an acid catalyst has the ability to produce biodiesel from low-quality oil containing significant FFA and water. Alkaline catalysts are better in promoting the formation of methoxide anion from methanol

Table 2. Various mixed metal oxide catalysts reported for biodiesel production

SL. No.	Catalyst	Feedstocks	Condition[a]	Conversion (%) / Yield (%)	Ref.
1	K_2SiO_3/AlSBA-15	JCO	9 : 1, 3, 60, 2.5	95 (Y)	46
2	La_2O_3/ZrO_2	Sunflower oil	30 : 1, 21, 200, 5	84.9 (Y)	44
3	Na_2ZrO_3	Soybean oil	6 ; 1, 3, 65, 3	98.3 (C)	48
4	MgO-ZnO	JCO	25 : 1, 3, 120, 3	83 (Y)	45
5	LaMgO	Cotton Oil	54 : 1, 5, 65, 20 (mins)	96 (C)	49
6	TiO_2–MgO	WCO	50 : 1, 10, 160, 6	92.3 (Y)	50
7	CaO–CeO_2	Rapeseed oil	6 : 1, 10, 60, 10	90 (Y)	51
8	SrO/SiO_2	Olive oil	6 : 1, 5, 65, 10 (mins)	95 (C)	52
9	Mixed oxides of Zn and Al	Soybean oil	45 : 1, 5, 182.5,	86 (C)	53
10	CaO–ZnO	Palm kernel oil	30 : 1, 10, 60, 1	>94 (Y)	54
11	TiO_2–ZnO NPs	Palm oil	6 : 1, 14, 60, 5	98 (C)	58
12	MgO-Li_2O NPs	Refined Soybean oil	30 : 1, 60, 6	96.2 (C)	59
13	MgO–ZrO_2 NPs	Soybean oil	20 : 1, 3, 150, 6	99 (Y)	60
14	$Sr_3Al_2O_6$ NPs	Soybean oil	25 : 1, 1.3, 60, 1	95.7 ± 0.5 (C)	61

[a] MTOR, catalyst loading (wt. %), temperature (°C), time (h).

in the transesterification reaction. Acidic catalysts, on the other hand, are less active in the formation of methoxide anion, but they can promote transesterification by activating carbonyl bonds via H^+ addition (Brønsted acidic sites) or coordination of carbonyl oxygen with coordinatively unsaturated metal ion sites (Lewis acidic sites). As a result, when the number of Brønsted or Lewis acidic sites increase it promotes rapid transesterification of FAME. Heterogeneous acid catalysts are praised as a viable alternative to homogeneous acid catalysts since they have a number of advantages. These advantages include their simplicity of separation and reuse, as well as their lesser corrosiveness and toxicity.[63] Many research groups have explored the efficacy of solid acid catalysts for esterification/transesterification processes in recent years, and suggested cost-effective and environmentally friendly biodiesel manufacturing methods.[64,65]

Acid functionalized metal oxide

Table 3 shows the different acid functionalized metal oxides; among the solid acid catalysts, the sulfated catalysts have gotten a lot of interest for transesterification because of their super-acid natureChemically stable sulfated inorganic metal oxides with super acidity comparable to 100% sulfuric acid, exceptional acid–base, and redox characteristics have been described.[66] Phosphotungstic acid-loaded KIT-5, sulfated zirconia, 12-Tungstosilicic acid anchored to SBA-15, tin oxide, Silicotungstic acid anchored to KIT-6, and 12-Tungstophosphoric acid (TPA) were all used in biodiesel production.

Using acid-loaded KIT-5 mesoporous material, researchers investigated acid-catalyzed transesterification to make algae biodiesel. Under the optimal reaction condition, MeOH : Oil of 1 : 2 in the presence of 1.5 wt % mesoporous acid catalyst, 60ºC, and a 6-hour residence time. With the application of a 35% phosphotungstic acid-based KIT-5 catalyst, almost 98% biodiesel conversion was accomplished under ideal conditions. There observed a progressive decline in FAME conversion when the catalyst was regenerated.[67]

In the meantime, Muthu *et al.*[68] used a sulfated zirconia (SZ) catalyst for FAME production from neem (*Azadirachta indica*) oil. SZ is prepared using solvent free method. Solid acid catalysts have been found to be suitable for oils with a high FFA content and to have good stability. The final alkali catalysed (1% KOH) transesterification with methanol for biodiesel production uses the first-step product, which has an acid value of less than 2. The yield of biodiesel from this process is 95%. The catalytic activity of solid acid catalysts in the transesterification is influenced by strong acid sites. The catalyst was known to be remarkably stable in oils with high FFA concentrations. The strong acid sites of this catalyst showed a considerable impact on its reactivity in the transformation of neem oil.

Narkhede *et al.*[69] synthesised biodiesel from waste cooking oil using a 12-tungstosilicic acid catalyst impregnated over the mesoporous SBA-15 support. With a waste 8 : 1 MTOR, 0.3 wt. % catalyst loading, and a reaction temperature of 65ºC for a 8 h reaction time, the highest FAME concersion 86% was achieved. The present catalyst's large surface area and pore dimension play an important role in the dispersion of large triglyceride molecules onto the catalyst's surface. The acid sites of the catalyst combine with the carbonyl oxygen to form the carbocation. Heteropoly acids are known to help speed up the reaction by stabilising the carbocation intermediate. After several experiments, it was observed that the catalyst's stability and activity had not changed significantly, and elmemtal analysis (EDX) confirmed that there were no significant leaching in FAME conversion for multiple run.

Changmai *et al.*[56] created a magnetically recoverable $Fe_3O_4@SiO_2\text{-}SO_3H$ core@shell nanoparticulate acid catalyst via a sequential co-precipitation, coating, and functionalization procedure. As a heterogeneous catalyst, it was utilised to simultaneously transesterify and esterify triglycerides and free fatty acids in Jatropha curcas oil (JCO) to a fatty acid methyl ester (FAME) combination. Under the optimised reaction conditions of 9:1 MTOR, catalyst loading 8 wt. %, reaction temperature 80ºC, for 3.5 hours, FAME conversion 98.1% was achieved The reusability of the catalyst after 9 cycles revealed 81% FAME conversion. The decline in conversion was influenced by a mixture of methylation of the active sulfonic acid groups and leaching, as confirmed by electron microscopy/elemental analysis.

In this context, Gardy *et al.*[70,71] reported a simple method for making a sulfated doped TiO_2 catalyst, the authors claim that the produced catalyst has higher reactivity than other sulfated metal oxides, owing to the acidic properties of TiO_2 particles that were sulfonated to increase their acidity. By expanding the pore volumes/sizes of the nano-catalyst, the one-pot post-surface functionalisation method with hydrophilic functional groups ($-SO_3H$) was also observed to boost the acid strengths of the nano-catalyst, As a result, there are more acid sites for the reactants and methanol is more accessible to the triglycerides (TG)/free fatty acids (FFAs). The catalyst performed admirably in the synthesis of FAME from WCO.

Bala *et al.*[72] used silicotungstic acid anchored to mesoporous siliceous support (KIT-6) as a catalyst for biodiesel production. On high FFA-containing feedstock, the catalyst's efficiency was tested. At 70 ºC, 2:1 MTOR, catalyst loading 1.2 wt. % and 3 h constant stirring, KIT-6 containing 26 wt. % silicotungstic acid performed best for transesterification. After calcination, esterification, and recycling, the catalyst was found to be stable. It was also found that the concentration of silicotungstic acid in the catalyst has a significant impact on conversion efficiency. The large surface area of the support improves catalyst stability at temperatures within the bulk HPA's stability range. Recyclability of catalyst after 4 run, resulting in a 26 % reduction in conversion. A small amount of acid leaching from the catalyst effect the decrease in activity. Leaching can be avoided by ageing the catalyst at a higher temperature, but the catalyst's overall activity may be compromised as a result.

Singh and Patel[73] investigated the use of mesoporous molecular material (MCM-48, mobile composition of matter) supported by 12-tungstophosphoric acid (TPA) for biodiesel production by esterification of oleic acid with methanol. The biodiesel conversion increased as the loading of TPA on MCM increased, which could be due to the increase in total acidity. Due to the rise in catalytically active sites, conversion increased as the catalytic concentration increased. Under the optimal condition 6 wt. % catalyst loading, 8:1 MTOR and 65ºC reaction temperatue for 16 h reaction time with stirring at 800 rpm 93% and 95%, for JO and WCO, FAME conversions was obtained respectively. TPA species were not discharged from the carrier (MCM-48), according to tests. The reusability studies indicate that using the redeveloped catalyst for up to 4 runs, there was no significant change in the conversion of oleic acid.

Soltani *et al.*[74] used a SO_3H group-functionalized mesoporous zinc oxide catalyst to study the esterification of palm fatty acid distillate (PFAD) (SO_3H-ZnO). Postsulphonation operations were used to functionalize a hydrothermally produced mesoporous ZnO catalyst. Under the optimized conditions of 2 wt. % catalyst, 9 : 1 MTOR, 90 mins reaction time and 120ºC temperature, giving PFAD conversion 95.60%. The synthesised mesoporous SO_3H-ZnO catalysts had a high surface area of 305.62 m^2g^{-1} and a pore diameter of 3.16 nm, allowing acid functional groups with high density to reach the active sites more easily. On the catalyst sites, FTIR analysis revealed the presence of functional groups such as –OH, –COOH, and $–SO_3H$.

Khayoon and Hameed[75] performed a single-step transesterification of high FFA content crude Karanj oil (CKO) and methanol using a variety of solid acid catalysts based on molybdophosphoric acid (MP, 5–25 wt. %) on SBA-16 support. The experimental studies found that MP-S-16(15) with 15 wt. % MP has the highest catalytic activity and enabled the FAME conversion of 81.8%. Upon 220ºC thermal treatment the catalyst MP-S-16(15) maintained the Keggin structure which was confirmed by XRD and FT-IR characterization. A result, over the catalyst surface, the MP Keggin anions were the active species. The MP-S-16(15) catalyst's catalytic performance can be attributed to the large pore size and strong acidity, which aided substrate and product diffusion.

Furthermore, Pereira *et al.*[76] showed that the SnSO4 catalyst can be used to esterify oleic acid (as a model feedstock) and acid soybean oil with high FFA content. Using excess ethanol and 5 wt. % $SnSO_4$ at 100°C for 3 hours, it was observed that the model feedstock containing 70 wt. % FFA and FAME conversion 92%. Furthermore, the catalyst was noted to be stable for ten cycles with no significant decrease in FAME conversion. As a result, the solubility of $SnSO_4$ in the reaction medium was also attributed to its catalytic activity. Esterification efficiency was higher with $SnSO_4$ than with $SnCl_2.2H_2O$, owing to the presence of more H^+ ions in the medium.

Xie *et al.*[77] investigated phenylsulfonic acid-functionalized SBA-15 silica as an active catalyst for the esterification of FFA present in oils with methanol. In 5 hours at 67°C, 96.7% of FFA was converted to methyl esters using 7 % catalyst and a 15 : 1 molar ratio of methanol to oil. The esterification activity of phenyl SBA-15 was changed after it was sulphonated, indicating that SO_3H groups act as proton donors in the esterification reaction. As a result, after several cycle the reused catalyst maintained good stability and no significant decrease in FFA conversion. Surface adsorption of intermediates and products likely caused a small loss.

In another work, Wang *et al.*[78] used a novel one-pot synthesis approach to obtain a solid super acid catalyst, $S_2O_8^{2-}/ZrO_2$, using ammonium persulfate and vapour phase hydrolysis. The prepared catalyst was used to make biodiesel from stale soybean oil. Under muffle furnace at 500°C when $S_2O_8^{2-}/ZrO_2$ was heated, TEM (transmission electron microscopy) revealed the tetragonal phase ZrO2 microcrystallites XRD while characterization revealed the amorphous phase. The microcrystallites with more $S_2O_8^{2-}$ contained more super acids and had higher transesterification catalytic activity under smooth reaction conditions. Under the optimised condition of Temperatures of 20:1 MTOR, temperature 110 °C and reaction time 4 h, 100% biofuel selectivity and soybean oil conversion were obtained. The catalytic performance of sulphated zirconia in aqueous media degraded with reuse, which was attributed to hydrolysis. With cyclic utilisation, no sulphur leaching was noted in the biodiesel.

Mixed metal oxide

A variety of acidic mixed metal oxide catalysts have been employed to offset the issue of elevated FFA glad in cut-price biodiesel feedstock used in FAME output (Table 4). In order the esterification of PFAD and methanol, ZrFeTiO, ZrFeO, and FeTiO catalysts were employed.[80] The presence of Ti in wt. % was discovered during analysis, indicating that the produced catalyst was very acidic. Though all catalysts showed strong catalytic activity in PFAD esterification with methanol, ZrFeTiO calcined at 600°C for 4 h after 5 h of reaction at 170°C, 3 wt. % catalyst, and a 3 : 1 methanol/oil ratio yielded the highest yield to methyl esters, 96.54%. ZrFeTiO's enhanced catalytic activity was attributed to its high acidity and better textural qualities due to the addition of Zr during the preparation process. The catalyst was repeated and judged stable because leaching of active components had little effect on its activity.

Suzuta *et al.*[81] described a heterogeneous catalyst, $Fe_2O_3–SiO_2$, that was synthesised by pore-filling and used to convert JCO to FAME. The initial SiO2 was also evaluated without the addition of Fe. Under reaction conditions of 200°C, 3 h, and 15 wt. % catalyst, a FAME yield of 45 % was produced. The acidity of the catalyst increased dramatically when the Fe loading was increased from 0.07 to 2.1 wt. %,

Table 3. Various acid functionalized solid catalysts reported for biodiesel production

Sl. No.	Catalyst	Feedstocks	Condition[a]	Conversion (%) / Yield (%)	Ref.
1	Phosophotungstic acid-loaded KIT-5	Algal oil	2 : 1, 1.5, 60, 6	98 (C)	67
2	SO_4^{2-}/ZrO_2	Neem oil	9 : 1, 1, 65, 2	95 (C)	68
3	12-Tungstosilicic acid anchored to SBA-15	WCO	8 : 1, 0.3, 65, 8	86 (C)	69
4	$Ti(SO_4)O$	WCO	9 : 1, 1.5, 75, 3	97.1 (Y)	70
5	$Fe_3O_4@SiO_2$-SO_3H	JCO	9 : 1, 8, 80, 3.5	98±1 (C)	56
6	$TiO_2/PrSO_3H$	WCO	15 : 1, 4.5, 60, 9	98.3 (C)	71
7	Silicotungstic acid anchored to KIT-6	Algal oil, WCO	2 : 1, 1.5, 70, 3	NP	72
8	12-Tungstophosphoric acid (MCM-48)	JCO	1 : 8, 6, 65, 16	>90 (C)	73
9	SO_3H-ZnO	PFAD	9 : 1, 2, 120, 1.5	95.6 (Y)	74
10	MP-anchored SBA-16	Karanja	8 : 1, 1.7, 140, 5	82 (Y)	75
11	$SnSO_4$	Soybean oil	3.5 : 1,5, 100, 3	92 (Y)	76
12	SO_4^{2-}/TiO_2	Rapeseed oil	20 : 1, NR, 80, 12	51 (C)	79
13	Phenylsulphonic acid-functionalized SBA-15	Vegetable oil	50 : 1, 7, 67, 5	96.7 (C)	77
14	$S_2O_8^{2-}/ZrO_2$	Expired soybean oil	20 : 1, 3, 110, 4	100 (C)	78

[a]MTOR, catalyst loading (wt. %), temperature (°C), time (h).

and at 7.1 wt. % Fe loading, the maximum >97.0 % biodiesel conversion was reached under the optimum reaction conditions. The active sites were identified as Fe-oxide species dispersed across the SiO_2 surface. However, the Fe_2O_3–SiO_2 catalysts' acidic activity was proven to promote the FAME production reaction.

The transesterification of soybean oil with methanol to fatty acid methyl ester (FAME) was carried out by Xie *et al.*[82] utilising WO_3/SnO_2 solid as a heterogeneous acid catalyst. The greatest catalytic activity was found in a WO_3/SnO_2 catalyst made by an impregnation approach with a WO_3 loading of 30% and calcined at a temperature of 1173 K. When 30 : 1 M methanol to oil ratio and 5% catalyst were used, the maximum FAME yield of 79.2% was attained after 5 hours at 383 K. Without severe deactivation, the solid catalyst can be reused for four runs.

In a batch process using ethanol and methanol solvents, a zinc aluminate catalyst ($ZnAl_2O_4$) was employed to transesterify waste frying oil. With a 40 : 1 MTOR, a temperature greater than 150°C, a residence duration of 2 h, a stirrer speed of 700 rpm, and changing catalyst loading in the range of 1–10 wt. % of the initial volume of oil, more than 95% ester conversion was achieved. The catalyst was recovered and reused three times, but the yield decreased after the third, possibly due to carbon deposition on the catalyst surface or the loss of small catalyst particles during the recovery process. Despite the presence of both acidic and basic sites, the catalyst had a regular spine-like structure with acidic character.[83]

According to Thirunavukkarasu *et al.*[84] when Zn $(NO_3)_2$ is impregnated on Al_2O_3 and Fe_2O_3 and calcined at 873K, crystalline spinel phases of $ZnAl_2O_4$ and $ZnFe_2O_4$ develop readily on the surface. Both the catalysts $ZnAl_2O_4$ and $ZnFe_2O_4$ are active in the transesterification of vegetable

Table 4. Various mixed metal oxide solid catalysts reported for biodiesel production

Sl. No.	Catalyst	Feedstocks	Condition[a]	Conversion (%) / Yield (%)	Ref.
1	ZrFeTiO	PFAD	3 : 1, 3, 170, 5	96.54 (Y)	80
2	Fe_2O_3–SiO_2	Jatropha oil	218 : 1, 15, 220, 3	95.6 (Y)	81
3	WO_3/SnO_2	Soybean oil	30 : 1, 5, 110, 5	79.2 (Y)	82
4	$ZnAl_2O_4$	Waste frying oil	40 : 1, 1-10, 150, 2	>95 (C)	83
5	$ZnAl_2O_4/ZnFe_2O_4$	Sunflower oil, WCO, Jatropha oil	9 : 1, 5, 180, 10	>90 (Y)	84
6	$Cs_{1.5}H_{1.5}PW_{12}O_{40}$	JCO	25 : 1, 2.9, 65, 35 (mins)	>90.5 (Y)	85
7	WO_3 (30 wt. %)/ $ALPO_4$	Soybean oil	30 : 1, 5, 180, 5	72.5 (Y)	86
8	$Mn_xZr_{0.5y}Al_xO_3$	WCO	14 : 1, 2.5, 150, 5	>93 (Y)	87
9	SnO_2/SiO_2	Soybean oil	24 : 1, 5, 180, 5	81.7 (Y)	88
10	Zr-Mo	Oleic acid	10 : 1, 4, 180, 2	94.2 (C)	89
11	FMWMo	WCO	25 : 1, 6, 200, 8	92.3 ± 1.12 (Y)	43
12	Fe–Mn–MoO_3/ZrO_2	WCO	25 : 1, 4, 200, 5	95.6 ± 0.15 (Y)	90
13	$SO4^{2-}/TiO_2$–SiO_2	Waste soybean oil	20 : 1, 10, 120, 3	88 (Y)	91

as

[a] MTOR, catalyst loading (wt. %), temperature (°C), time (h).

oils (sunflower, Jatropha, and waste cooking oils), X -ray valence band spectroscopy (XVB) revealed that Zn 3d electrons were likely to play a significant role in the electronic excitation of the spinels ($ZnAl_2O_4$ and $ZnFe_2O_4$) during the reaction. As a result, electron densities of Zn ions are thought to have had a role in the transesterification activity of the spinel samples investigated.

Using ultrasonic irradiation, raw JO was transesterified using a cesium-doped heteropolyacid catalyst. $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ demonstrated the highest FAME generation of 81.3 % in 1 hour among the four Cs-based heteropolyacid catalysts with varying Cs exchange levels. Increases in Cs levels resulted in decreased catalyst activity. At a molar ratio of 1.5, the Cs-exchanged tungstophosphoric acid (TPA; $H_3PW_{12}O_{40}$ nH_2O) catalyst had the greatest effect on the reaction yield. With a 25 : 1 MTOR and a residence time of 34 minutes at 60 percent ultrasonic amplitude, the highest yield of 90.5% was achieved. The catalyst's reactivity was minimally reduced in multiple subsequent reaction runs.[85]

$WO_3/AlPO_4$ catalysts produced by impregnating $AlPO_4$ with ammonium metatungstate are also studied by Xie *et al.*[86] and found that a $WO_3/AlPO_4$ catalyst with a 30 wt. % WO_3 loading had moderate to outstanding reactivity for transesterification and esterification, as well as a high FAME production of 72.5% after 5 hours at 180ºC. The inclusion of WO was said to boost the acid sites on the catalyst's surface, resulting in good catalytic activity. Over four transesterification cycles, the catalyst remained stable, losing only 4% of its activity.

For the transformation of WCO to FAME, Amani *et al.*[87] reported a series of $Mn_{3.5x}Zr_{0.5y}Al_xO_3$ catalysts. The $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalyst has higher catalyst reactivity (>93 %) than the $Mn_{1.4}Zr_{0.35}O_3$ catalyst in terms of FAME production (52.8%). The reactivity of the catalyst was effectively affected by the bonding between metals in the crystal structure. Although Mn alternated the shape and catalyst basic site density, the amphoteric component of the Al developed the surface region of the catalyst and framed a complex structure with other metal oxides.

Xie *et al.*[88] produced a SnO_2–SiO_2 acid catalyst by coating SiO_2 with 8 wt% Sn and calcining it at 550°C. With a methanol/oil molar ratio of 24 and a temperature of 180ºC, the developed catalyst (5 wt. %) yielded 81.7 % FAME from transesterification of soybean oil with methanol after 5 hours. The amorphous SnO_2 particles on the silica support were shown to be catalytically active for both the transesterification and esterification of FFA, providing a high FFA yield of 94.6%. Furthermore, the SnO_2/SiO_2 catalyst could be easily recovered and reused for at least four cycles without significant loss of catalytic activity.

In this line, Zhang *et al*[89] studied various Zr-Mo based mixed metal oxide solid acid catalyst for biodiesel production. A series of functionalized carboxylic acid such as myristic acid, stearic acid, lauric acid and palmitic acid. The addition of such monofunctional carboxylic acids to the Zr–Mo metal oxide improves the acidity and surface area of the catalyst, increasing the reaction rate. They also found that the stearic acid-functionalized Zr–Mo metal oxide had the greatest results of all the catalysts, with a maximum oleic acid conversion of 94.2%. Furthermore, the mixed-oxide catalysts could be reused up to six times without losing catalytic activity.

Alhassan *et al.*[43] investigated the preparation of a solid ferric manganese dopped tungstated molybdena nanoparticle catalyst by impregnation, followed by calcination at 600°C for 3 h and use in biodiesel production with WCO. The FAME yield of transesterification reaction from tungstate molybdena and ferric manganese dopped tungstate molybdena were 65.00.17 and 92.31.12, respectively. Ferric manganese dopped tungstate molybdena has a higher pecific surface area, density of the active centre and overall higher in biodiesel yield, showing that the ferric manganese dopants increase the acidity, catalytic activity and surface area of ferric manganese dopped tungstate molybdena catalysts compared to tungstate molybdena catalysts.

Similarly Alhassan *et al.*[90] synthesized Fe–Mn–MoO_3/ZrO_2 catalyst for biodiesel production via fry vegetable oil. The catalyst was prepared by impregnation reaction followed by calcination at 600 °C. Under the optimum condition 4 wt. % catalyst loading, 25 : 1 MTOR, 200°C temperature for 5 h reaction time the FAME yield of 73.0±0.25, 95.6±0.15 % was obtained for molybdated zirconia and ferric manganese doped molybdated zirconia respectively. The addition of ferric manganese doped resulting in higher surface area, increasing catalytic activity and density of the active centers and overall increased the FAME yield in ferric manganese doped molybdated zirconia compared to the relative molybdated zirconia catalysts. Reusability of the catalyst show no leaching of manganese and insignificant leaching in the iron and molybdenum after seven cycle.

Furthermore, Shao *et al.*[91] prepared SO_4^{2-}/TiO_2-SiO_2 catalysts by the sol–gel method, biodiesel yield of 93.7 % was achieved. the catalytic activities of the TSC-550 and S-TSC-450 catalysts in the FAME conversion attempted at the same reaction conditions showed that the activities of S-TSC-450 was far much greater than that of the TSC-550 93.7% and 29.6% respectively. The S-TSC-450 has more proton sites, and the sulphate group is well linked to the composite, resulting in stable solid acids. Furthermore, the high activity found here could be ascribed to the high acidity aided by the presence of the sulphate group, the large surface area, and the presence of the sulphate group. This chemical has a morphological and meso structure that facilitates the adsorption of reactant molecules. Because of their ease of separation from the reaction mixture and reusability, sulfated metal oxides are preferred for consumption.

Overall, acidic functionalized metal oxide and acidic mixed metal oxide catalysts showed good performance toward biodiesel production. One of the advantages of using acidic metal or mixed metal oxide catalyst is that it can catalyst esterification and transesterification reaction without soap formation as a by-product. The methanol-to-oil molar ratio, concentration of the catalyst, stirring speed and reaction temperature, were found to be particular for distinct catalysts in order to achieve maximal biodiesel yield and conversion of the corresponding oil. For repeated cycles, the majority of the basic mixed metal oxide catalysts performed well.

Conclusion

Transesterification of vegetable oil for biodiesel assemble employed of heterogeneous catalysts is greatly suppress by the catalyst preparation technique, adopted precursors, and beginning of oil. The material's acidic and basic characteristics were thought to be critical for successful catalysis. Due to highly reactive, affordable and readily available, several metal oxides such as alkali and alkaline earth metals are often employed as heterogeneous catalysts for offering of biodiesel. The catalytic action of various basic and solid acid catalysts was analysis for several oils in various reaction circumstances in this review. The MTOR, catalyst loading, reaction temperature and reaction time were found to be particular for distinct catalysts in order to achieve maximal biodiesel yield and conversion of the corresponding oil. For repeated cycles, the majority of the heterogeneous catalysts performed well.

The current findings showed that the catalyst's characteristics (like, acidity and basicity) are critical in the production of biodiesel. According to several studies, the basicity of the catalyst is corelated to the transesterification exploit. Likewise, the esterification activity of the catalyst is determined by its acidity. As the acidity of the catalyst rises, so does the esterification activity also increased. In addition to its basicity and acidity, catalytic activity of a solid catalyst is determined by its porosity and surface area. According to studies, the catalyst's having high surface area increases the biodiesel production rate.

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