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Abstract: Biodiesel production through heterogeneous catalyzed reaction has emerged as a preferred route as it is environmentally friendly, needs no water washing, product separation is much easier, hence reducing process stages. This review has discussed the advancement in research and development related with heterogeneous catalysts used for biodiesel production. The heterogeneous base catalysts have shown to be effective for biodiesel production, although have the limitation of being sensitive to high free fatty acid feedstocks and water content of feedstocks. Solid acid catalysts are capable of esterifying high free fatty acid feedstocks with the presence of acid catalytic active sites. However, heterogeneous acid-base (bifunctional) and strong solid acids catalysts are potential catalysts for biodiesel production as they show the ability to simultaneously catalyze esterification and transesterification reactions. Solid catalysts with presence of acid and base catalytic sites prove to be the best for production and the use of nanocatalyst is also encourage as it will boost the catalyst properties which is responsible for high yield of biodiesel. Furthermore, this review will help in the selection of suitable catalysts and optimum conditions for biodiesel production

Keywords: Biodiesel, Heterogeneous catalyst, Transesterification, Esterification, High free fatty acid feedstocks

Introduction

The fact that fossil fuel supply is limited, due to the depletion of reserves and the high energy demand in an industrialized nations of the world, the domestic sector and the problem of pollution caused by widespread usage of fossil fuel, the search for an alternative renewable energy source became necessary. According to an annual forecast by the United States (U.S.) Energy Information Administration, considering the raise in population and economic growth in developing countries, by the year 2035, the world will be more dependent on fossil fuels than ever it finds (Arumugan, 2010). In recent decades, biodiesel has been found to be a promising source, an alternative diesel fuel from renewable sources with better advantages, and can serve as a substitute for fossil diesel oil without any needed modification of the existing engine system (Leung et al., 2010).

Biodiesel has some advantages over petroleum based diesel fuel such as it produces less smoke, show a favorable combustion emission profile, lower emission of carbon monoxide, sulfur dioxide and uncombusted hydrocarbon and easy biodegradability (Borges & Díaz., 2012). It is worthy to note that biodiesel is considered the fastest growing industry worldwide (Sani et al., 2014).

Many vegetable oils types have been used as feedstock for biodiesel production and these include sunflower, soybean, rapeseed etc. The major setback of using vegetable oil feedstock is the high price of combustible vegetable oils compared to that of fossil diesel fuel. Due to this fact, non-edible oils such as *Jatropha* (Tiwari et al., 2007), waste cooking oils (Kefas & Kovo, 2022; Wang et al., 2007), crude cotton seed oil (Mujeli et al., 2016) or palm fatty acid distillate (PFAD) (Kefas et al., 2018) are preferred for the production of biodiesel as a result of their low price (Zabeti et al., 2009). In recent times, raw material obtained from algae and other renewable feedstock has been used to produce biodiesel to provide sustainability to properly justify the biodiesel industry (Canakci & Vangerpen, 1999; Sharma et al., 2011).

The most common method to produce biodiesel is the transesterification due to its simplicity and industrial usage. Other methods are: thermal cracking (pyrolysis), direct use of vegetable oil, and micro emulsions (Helwani et al., 2009). When thermal cracking and micro emulsion methods are used to produce biodiesel, it leads to incomplete combustion in engine due to low cetane number. Also biodiesel obtained from direct use of vegetable oil has a high viscosity property which can damage the diesel engine when applied. Biodiesel is most commonly produced by transesterification of triglycerides found in vegetable oils and animal fats with alcohol (methanol) in the presence of a base or acid catalyst to form fatty acid methyl esters (FAME) and glycerol (Sebayang et al., 2010)1 .When the transesterification reaction with alcohol occurs, the first step is the triglycerides to diglycerides conversion, which is followed by the subsequent higher glycerides to lower glycerides conversion and then to glycerol, yielding one methyl ester molecule from each glyceride at each step (Banerjee & Chakraborty, 2009; Vyas et al., 2010).

Various alcohol types have been used in the production of biodiesel such as methanol, ethanol, propanol and butanol. Although, the most widely used are methanol and ethanol. However, methanol is the commonly used alcohol for the production of biodiesel because of its low cost and industrial availability (Lam et al., 2010). When the alcohol, methanol is used for the transesterification reaction, the resultant product will be a fatty acid methyl esters mixture (FAME), and a fatty acid ethyl esters (FAEE) results, if ethanol is used as reactant for the reaction.

The main function of the catalyst in transesterification reaction is to increase the rate of reaction and the methyl esters yield. In general catalyst can be categorized, namely acids, alkalis and enzymes (Shimada et al., 1999). The alkali and acid catalysts are either homogeneous or heterogeneous by nature. Looking at their chemical presence, homogeneous catalysts act usually as liquid in the liquid phase, whereas heterogeneous act as solid, in a different phase from the reaction mixture. The use of heterogeneous catalyst for the synthesis of biodiesel has

been a relatively recent area of research. This is due to the fact that homogenous catalysts used for biodiesel production presents a few disadvantages such as washing of biodiesel with water to remove the catalyst resulting in waste water generation and loss of biodiesel. Heterogeneous catalysts have the advantage of easy separation from product and reusability (Sharma et al., 2011). Solid (heterogeneous) base catalysts have been successful with high yield of biodiesel obtained due to more activeness requiring relatively shorter reaction time and lower reaction temperature (Borges & Daiz., 2012).. However, they are sensitive to feedstock with high free fatty acids (FFA) content such as non-edible oils and waste cooking oils. Thus solid acid catalysts are preferred as they are insensitive to FFA and water content of feedstock as well as can simultaneously catalyze esterification and transesterification reactions. In addition to their reusability and easy removal, solid acid catalyst does not cause corrosion of process equipment as found with some acid homogeneous catalysts like sulfuric acid (Sani et al., 2014). Although, heterogeneous catalysts have some few disadvantages such as high temperature, long reaction time and leaching but can be minimized during catalyst preparation.

Excellent review papers on solid catalysts are available (Helwani et al., 2009; Islam et al., 2014; Avhad & Marchetti, 2016; Alemu & Alemu, 2023; Mohamed et al., 2024). Solid catalysts that can be used for transesterification reaction are namely acidic type, basic type and bifunctional type (acidic-basic type). Presently research trends are moving toward the search for new solid catalysts that can simultaneously carryout esterification and transesterification reaction steps. Hence this review focuses on recent research and advancement related to several solid catalysts used for production of biodiesel, performing simultaneously esterification and transesterification reaction. In addition, acid esterification and base transesterification, optimal reaction conditions and yield/conversion are also included.

Heterogeneous Catalyst for Biodiesel Production

Biodiesel can be produce in two ways that is in one or two step processes as shown in Fig. 1. Heterogeneous catalysts are catalysts that exist in different phase with the reactant or product (Mardhiah et al., 2017; Pandit et al., 2023; Mohamed et al., 2024). These groups of catalysts are broadly employed in the biofuel industry due to the limitations of homogeneous catalysts such as high-cost and post separation processes.

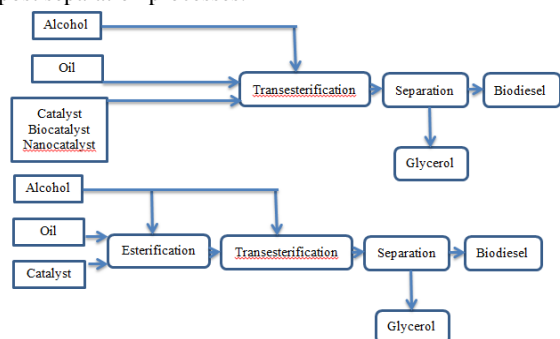


Figure 1: One and two step process for biodiesel production
Heterogeneous catalysts are able to simplify the biodiesel production process, in which no soap formation occurs,

easy separation step and high reusability of the catalyst, making the overall process more recyclable and sustainable (Mardhiah et al., 2017). Therefore, as a result of the advantages of these groups of catalysts make it preferable employed in biodiesel production.

Heterogeneous Base Catalyst for Transesterification Reaction

In recent years, transesterification reaction to produce biodiesel using base catalyst is the most extended process. Some reviews about solid basic catalysts have been reported (Borges & Daiz, 2012; Sharma et al., 2011; Helwani et al., 2009). However, more recent effective catalysts for obtaining high FAME conversion at low reaction temperatures are discussed below. These types of solid catalysts are categorized as alkaline earth metal hydroxides, alkaline metals carbonates, alumina loaded with different compounds, hydrotalcites, basic zeolites and many other compounds with a high basic properties (Encinar et al., 2005; Sharma et al., 2011; Verziu et al., 2008)..

Metal Oxides

The most studied group of basic heterogeneous catalysts is the metal oxides. There are many metal oxides that have been studied in literatures which include calcium oxide, strontium oxide, magnesium oxide, mixed oxides and hydrotalcites (Borges & Daiz, 2012). Among the metal oxide catalysts available, the most widely used is CaO due to its low toxicity, easy availability and cheap price (Lee et al., 2009). Additional advantages are high activity, long catalyst life and requires only moderate reaction conditions (Math et al., 2010). The fact that there is several natural calcium sources from wastes, like egg shells or mollusk shells, this made CaO to attract much attention. These shells are consisting of calcium carbonates which are calcined to produce basic calcium oxide that can be used as a catalyst for biodiesel production (Cho & Seo, 2010;).

The catalytic performance of the CaO egg shell from waste was compared to laboratory grade CaO in transesterification reaction. Wei et al., 2009 reported that the heterogeneous catalytic process by using 3wt% of calcined eggshell at 1000 °C for the trans-esterification of soybean oil, over 95% yield was obtained with 9:1 methanol to oil molar ratio, reaction temperature of 65 °C and 3 h of reaction time. The CaO catalyst was reused up to 13 times without any significant losing activity. Viriya-empikul et al., 2010 and Boey et al., 2009 noted that the egg shell-based catalyst has better catalytic activity in the trans- esterification of oil than mollusk shells. Viriya-empikul et al., 2010 concluded that catalyst surface area and calcium content are the main parameters that affect the egg shell-based catalyst's activity. Eggshell produces a more porous and higher surface in the case of calcium oxide as a result of the different calcium matrix organization; hence the catalytic activity of eggshell was better than mollusk. The good performance of eggshells among the waste selection in transesterification was reported by Viriya-empikul et al., 2012 that chicken eggshell contains the highest calcium and larger surface area as compared to golden apple snail and Meretrixvenus shell. Navajas et al., 2013 used waste eggshells for the transesterification of used cooking oil and obtained 100% yield of biodiesel using 4wt% catalyst load for 5h reaction time, while Niju et al., 2014 had used eggshells which underwent calcination–hydration–dehydration treatment to

obtain CaO catalyst. The transesterification of waste frying oil (WFO) with commercial CaO resulted in the conversion of 67.57% methylester whereas 94.52% was obtained for CaO derived from the calcination-hydration-dehydration treatment of eggshell at optimize condition of 5 wt% catalyst (based on oil weight), a reaction temperature of 65 °C, a methanol to oil ratio of 12:1 and a reaction time of 1h. Recently, Chen et al., 2014 reported CaO catalyst obtained from ostrich eggshell to yield up to 92.7% biodiesel using palm oil under the following conditions: methanol-to-oil ratio 9:1, catalyst load of 8wt%, reaction time 60min and ultra-sonic power 60% amplitude. In addition, the CaO catalyst was reused for more than 8 times without significant loss in catalytic activity. The several worked done on waste materials showed that to achieve a higher yield of biodiesel, a higher catalyst load and longer reaction time are needed (Tan et al., 2015).

Ho et al. 2014 developed a heterogeneous base catalyst from palm oil mill fly ash supported calcium oxide (CaO) catalyst and used for biodiesel synthesis from crude palm oil (CPO). The catalyst characterization tests showed higher surface area and basic sites which favored transesterification. The effects of process parameters namely; reaction temperature, methanol to oil molar ratio, catalyst loading and reaction time on biodiesel yield and fatty acid methyl ester (FAME) conversion were investigated. The results indicated a biodiesel yield and FAME conversion of 79.76% and 97.09%, respectively at optimized transesterification conditions of 45 °C reaction temperature, 12:1 methanol to oil molar ratio, 6 wt.% catalyst loading, 3 h reaction time and 700 rpm stirring speed. The developed catalyst was found to be feasibly reusable up to three consecutive cycles after regeneration by washing with methanol then recalcination at 850 °C for 2 h. The catalytic performance of sea sand as a nonconventional catalyst was studied by Muciño et al., 2014 in the transesterification reaction of used cooking oil and refined oil with methanol. Sea sand is known to have high content of CaCO₃ which was transformed into CaO by calcination. The catalyst produced biodiesel had 95.4% (polar + non polar methyl esters), 96.6% and 97.5% methyl esters content using used cooking oil, safflower oil and soybean oil, respectively. The optimized conditions for the biodiesel obtained are reaction temperature of 60 °C, 12:1 molar ratio of methanol: oil, catalyst amount of 7.5% and reaction time of 6 h. However, calcium based catalyst have some limitations since they are not highly stable and leaching of Ca occurs in the reaction mixture. Hence, researchers on calcium based catalyst are giving attention on improving its stability for biodiesel production. Magnesium oxide produced by direct heating of magnesium carbonate or magnesium hydroxide has also shown to possess catalytic activity for biodiesel synthesis, although it has the weakest basic strength and solubility in methanol among group II oxides (Zabeti et al., 2009) MgO has been loaded with an active metal, in order to increase its basicity. A Li-doped MgO was prepared by Wen et al., 2010 and used for biodiesel production. The catalyst exhibited 93.9 % FAME yield at 60 °C using 12:1 methanol/oil molar ratio and 9 wt.% catalyst amount. The results showed that the addition of Li promoted the formation of strong basic sites, thus resulting in an FAME yield increase. Alternatively, potassium hydroxide impregnated MgO was prepared and used for the

transesterification of mutton fat (Mutreja et al., 2011). The basic strength of MgO increased by impregnation with 20 wt.% KOH and the transesterification of mutton fat resulted in 98% conversion in 20 min with 22:1 methanol to fat molar ratio at 65 °C.

When each component differs distinctly from each other of mixed-metal oxide systems and used as support can offer interesting range of properties Tantirungrotechai et al., 2010. Like the combination of alumina and magnesia can produce new acid-base properties. These acid-base properties of alumina rely so much on the synthesis conditions and post-synthesis treatment whereas; magnesia features a unique basic characteristic. Several M(II)/M(III) mixed oxides was prepared by Fraile et al., 2010 where M(II) was Mg or Zn and M(III) was Al, Ga or La. These catalysts were tested in the transesterification of sunflower oil with methanol and transesterification of methyl palmitate with isobutanol. Results showed that the mixed oxides had strong basicity which was always linked to the presence of alkaline metals, not connected to the M (II) and M (III) nature. Series of Mg-Al mixed-metal oxides with Mg/Al ratios in the range 0.125–8 was synthesized via sol-gel by Tantirungrotechai et al., 2010. The base strength and activities of these mixed oxides were increased by impregnating with KI and tested for the transesterification of soybean oil. This KI impregnated Mg-Al mixed-metal oxide at 4:1 Mg/Al ratio, at 70 °C reaction temperature and after 8 h gave >90% conversion for transesterification reaction with methanol indicating was the most efficient catalyst. Ngamcharussrivichai et al., 2010 transesterified palm kernel oil with methanol over dolomite (mainly consisting of CaCO₃ and MgCO₃) solid base catalyst. The catalyst calcined at 800 °C resulted in aCa/Mg mixed oxide that showed activity for the formation of methyl esters at 60 °C reaction temperatures. The reusability of calcined dolomite was minor than for CaO. Ilgen, 2011 also studied the catalytic activity of dolomite. The transesterification of canola oil yielded over 90%FAME with calcinated (850 °C) dolomite when the reaction was carried out at methanol reflux temperature, with a 6:1 methanol to oil molar ratio, 3 h reaction time and a 1.5 wt.% catalyst amount. Taufiq-Yap et al., 2011 investigated calcium-based mixed oxides catalysts of CaMgO and CaZnO for the transesterification Jatropha curcas oil with methanol. Both catalysts were prepared by coprecipitation method with corresponding mixed metal nitrate solution in presence of a soluble carbonate salt. Comparing their catalytic activities with CaO, both CaMgO and CaZnO catalysts showed high activity as CaO with easy separation from the product. Besides, CaMgO was found to be more active than CaZnO having a higher than 80% conversion under transesterification conditions at 60 °C, 4 wt.% catalyst amount, 15:1 methanol to oil molar ratio and 6 h reaction time. Comparing the reusability, using CaMgO and CaZnO as catalyst exhibited slight decrease after sixth run in conversion, whereas Using CaO as catalyst conversion reduced significantly after forth run of reuse (Taufiq-Yap et al., 2011).

Hydrotalcites

Hydrotalcites or hydrotalcite-like compound are category of solid base catalysts, a layered of double hydroxide (LHDs) with general formula $[M^{2+}_{(1-x)}M^{3+x}(OH)_2]^{x+}(Ax/n)^{-n}.yH_2O.yH_2O$ have indicated to be an interesting and suitable catalyst for the transesterification reaction. The

hydrotalcite structure is based upon LHDs with brucite like ($\text{Mg}(\text{OH})_2$) hydroxide layers containing octahedrally coordinated M^{2+} and M^{3+} cations. The interest developed for transesterification oil with hydrotalcites catalyst is due to its strong surface basicity, pore volume and high surface area (Gao et al., 2010; Chantrasa et al., 2011). Navajas et al., 2010 studied some commercial Mg-Al hydrotalcites as catalyst for transesterification reaction and concluded that their catalytic activity was modest as compared with the results obtained from literature for hydrotalcites synthesized by co-precipitation method at laboratory scale. Furthermore, Silva et al., 2010 showed that further investigations on the optimization of experimental conditions using hydrotalcite catalysts were still needed in order to improve the process of biodiesel production as a result of high reaction temperatures required. Although, a good yield of FAME was gotten by Deng et al., 2011, when hydrotalcite particles as solid catalyst was used in transesterification reaction in an ultrasonic reactor. Also, high yield of FAME was gained by Gao et al., 2010 when KF/Mg-Ca hydrotalcite catalyst was used in the transesterification reaction of palm oil with methanol. Martins et al., 2013 used co-precipitation method to synthesized hydrotalcites with a Mg/Al molar ratio of 3.0 and the precursor was calcined at 450 °C for 6 h. Transesterification reactions were carried out in a jacketed reactor coupled to a condenser, with magnetic stirring at 64 °C under atmospheric pressure by varying the methanol to oil molar ratio and reaction time. High yield of 94.8% biodiesel was achieved from soybean oil with a methanol to oil molar ratio of 20:1, for 10 h and 5.0% catalyst (w/w).

Basic Zeolites

The physical and chemical properties, such as ionic interchange, adsorption and catalytic activity of basic zeolites make them applicable commercially for biodiesel production. Many researchers have studied the activity of zeolites in transesterification reaction because zeolites can serve as basic catalysts and generate weak active centers by interchanging with alkaline cations or reducing the silica/alumina ratio (Hattori, 1995). The occlusion of sodium metal clusters which increase the negative charge on the framework oxygen atoms improves the basicity of zeolites. Wet impregnation method, typically from a precursor solution are used to introduce the supported species into the zeolite pores (Davis et al., 2000). It was noted that there is a positive correlation between the yield of methyl esters and the number of basic sites on zeolites. Likewise, in transesterification reaction, calcination temperature is also relevant for determining the basic zeolites catalytic activity.

Wang et al., 2012 synthesis zeolite MCM-22 with colloidal silica and sodium aluminate and compared their efficiency with commercial Zeolite HY (CBV-780) in the transesterification of triolein. Both of the catalysts were microporous with large Brunauer Emmette Teller (BET) surface area with zeolites MCM-22 having an average size of 1-2 mm and CBV-780 was cube-like particulate with a dimension less than 1 mm. The maximum yield of 98% and 99% biodiesel was obtained irrespective of the great loss in BET surface area and deterioration of the crystalline structure when Na was exchanged with the ions on the surface of these zeolites. Soybean oil was transesterified with various catalysts, such as NaOx occluded in NaX (faujasite zeolite), K occluded in ETS-10 (titanosilicate

structure-10 zeolite) and ETS-10 (titanosilicate structure-10 zeolite) were studied (Suppes et al., 2004). More than 90% yield of methyl esters was achieved with oil to methanol molar ratio of 1:6 at different temperatures for 24 h and ETS-10 catalysts were found to be more effective than Zeolite-X type catalysts. Greater basicity of ETS-10 zeolites and their larger pore structures were responsible the increased conversion ratio of vegetable oil to methyl esters noticed. Introduction of alkali earth oxides and the molecular size of the metal oxide (Kovacheva et al., 2001) increased the amount of basic sites in the NaX zeolites, which led to the usage of nanocrystalline metal oxides as solid basic catalysts for biodiesel production. The transesterification of sunflower oil was investigated with the catalytic activity of CaO nanoparticles supported on NaX zeolites with methanol as solvent (Luz Martínez et al., 2011). Findings indicated that methyl ester content was noted to greatly depend on basicity of catalysts. The most effective catalyst was the one with 16% (w/w) CaO nanoparticles which had a conversion rate of more than 93.5%. However, only 5% of methyl esters content was achieved in the third cycle due to high loss in the catalytic activity of the catalyst confirming the hypothesis that metal species leach into the reaction mixture when they have a similar mechanism of homogeneous ones.

The main problem of the catalysts discussed is its unsuitability toward feedstock with high FFA content which can lead to soaps formation. An alternative to this regard is the use of two-step catalytic process where in the first step FFA is converted using an acid catalyst and a second step in which triglycerides is converted to FAME by a base catalyst. Also the use of bifunctional catalysts which can catalyze both FFA esterification reaction and triglycerides transesterification reaction at the same time can be a solution.

Heterogeneous Catalysts for Esterification Reaction

The high costs and limited availability of feedstock is a critical issue in the biodiesel industry. The cost of the vegetable oil alone takes up to 75 % of the total manufacturing cost making the production cost about 1.5 times than those of the petroleum diesel (Phan & Phan, 2008). To handle this situation, the use of non-edible vegetable oil and waste oils (such as waste cooking oil) will serve as an alternative feedstock, which reduces cost, since waste cooking oil (WCO) is 2 or 3 times cheaper than virgin vegetable oils (Phan & Phan, 2008). Besides, it helps in handling environmental problems resulting from waste vegetable oil disposal (Moraiz et al., 2010).

The main issue with the use of low cost feedstock is the large amount of free fatty acids which cannot be converted into biodiesel with a basic catalyst. The free fatty acids (FFA) react with the basic catalyst (neutralization reaction) resulting to soap formation, catalyst deactivation and low biodiesel conversion. Hence, there is a need to remove or convert FFA contained in used vegetable oil to FAME and should be join to biodiesel production process (Park et al., 2010).

When low-quality oils and fats are used as feedstocks, esterification reaction is usually carried out with homogeneous acid catalyst such as H_2SO_4 , HF, H_3PO_4 , HCl and p-toluene sulfonic acid (Carmo Jr et al., 2009), an alternative process to transesterification reaction. Although, the use these catalysts have hazardous and corrosive consequence. Therefore, considering environmental

problem and cost (Nascimento et al., 2011) heterogeneous acid catalysts can be considered as an alternative. The major advantage of solid acid catalysts is its ability to perform the esterification of free fatty acids, whereas the main advantage of solid base catalysts is its ability to perform the transesterification of triglycerides.

Many solid acid catalysts have been used for FFA esterification reaction such as: titanium oxide, zirconium oxide, tin oxide, sulfonic modified mesostructure silica, sulfonic ion-exchange resin, heteropoly acids (HPAs), and sulfonated carbon-based catalyst (Lam et al., 2010). Also used as heterogeneous solid acid catalysts are kaolins (Nascimento et al., 2011), raw halloysite (Zatta et al., 2011), WO_3/ZrO_2 (Park et al., 2010), ZnO/ZrO_2 (Kim et al., 2011), $\text{SO}_4^{2-}/\text{ZrO}_2$ (Rattanaphra et al., 2010), Ionic exchange resin (Tesser et al., 2010) and amberlyst (Son et al., 2010) but at high reaction temperatures.

This section gives a view of the recent research work related to heterogeneous acid catalysts studied in the esterification reaction to produce biodiesel at lower temperatures with high catalytic activities due to the presence of active acid sites (Gong et al., 2014; Liu et al., 2013; Lokman et al., 2015; Kefas et al., 2019).

12-tungstophosphoric acid (solid catalyst) was anchored to two different mesoporous silica supports namely MCM-41 and SBA-15 were synthesized in a study by Patel & Brahmkhathi, 2013, was characterized and used for biodiesel production through esterification of oleic acid with methanol. The operating parameters such as temperature, acid to methanol ratio, reaction time and catalyst concentration were optimized for maximum oleic acid conversion. 92 % (SBA-15) and 98 % (MCM-41) conversions were obtained at mild conditions of 60 °C reaction temperature with catalyst amount of 0.1 g. Both catalysts have strong bronsted acid sites making them active for the esterification of oleic acid. Liu et al., 2013 also utilized amino phosphoric acid resin D 418 solid catalyst in the esterification of stearic acid with ethanol. More than 90 % conversion of the esterification was obtained under microwave irradiation. Microwave assisted esterification compare to traditional heating requires lower temperature, less energy and ethanol additive. The conversion was achieved at a lower reaction temperature of 80 °C and time of 5 h.

Jeenpadiphat & Tungasmita, 2014 carried out a study on the esterification of oleic acid and high acid content palm oil with acid activated bentonite catalysts. Na-bentonite catalysts were acid-activated with either H_2SO_4 with concentration ranging from 0.25 to 2.0 M or with 0.5 M HNO_3 . The best catalytic activity was obtained with 0.5 M H_2SO_4 acid-activated bentonite yielding 100 % methyl oleate and 99 % FFA conversion in the esterification of pure oleic acid and palm oil oleic acid respectively. These conversions are higher than esterification using commercial amberlyst-15 catalyst. Acid activation of bent catalyst clearly increased the number of active sites.

Solid acid catalyst (PA-HPW) was prepared by modifying 12-tungstophosphoric acid by picolinic acid and used for the esterification of oleic acid with methanol (Gong et al., 2014). The solid acid catalyst (PA-HPW) showed good stability and high acidity for the esterification of mixtures, also during preparation and esterification, analysis indicated that there no decomposition of the kegging structure of the 12-tungstophosphoric acid. 100 %

conversion of oleic acid was achieved with the most active modified catalyst under optimized condition of 80 °C reaction temperature, 10:1 alcohol to acid ratio, 7 w% catalysts loading after 5 h. The possession of strong bronsted acid site was responsible for the excellent acid catalytic activity. The catalyst can be recovered and reused, hence a promising new type of heterogeneous catalyst.

Ong et al., 2014 studied the esterification of rubber seed oil containing 18 % FFA with carbon supported copper oxide (CuO/C) catalyst. The catalyst was characterized and the XPS analysis indicated the presence of CuO in the catalyst, also the acidity of the catalyst which is responsible for the higher activity was confirmed by Hammett indicator method. The conversion of FFA was about 95 % in 6 h, with reaction temperature of 65 °C, methanol to ratio of 10:1 and catalyst load of 8 w%. Compared to other heterogeneous catalyst, the CuO/C required lower methanol to oil ratio and lower temperature to obtain 95 % conversion. The catalyst could be recovered easily but it has a short life due to 13 % loss in activity after the first cycle.

Lokman et al., 2015 esterified palm fatty acid distillate with high FFA of 85 w% using sulfonated glucose derived acid catalyst. The catalyst was synthesized by sulfonating using concentrated sulfuric acid the incomplete carbonized D-glucose. The solid acid catalyst demonstrated a 95.4 % conversion of the FFA (92.3 % FAME yield) under optimized condition of 75 °C reaction temperature, 2.5 w% catalyst loading, and methanol to PFAD ratio of 10:1 after 2 h. the results indicated that the acid properties of the catalyst was enhanced by the attachment of the $-\text{SO}_3\text{H}$ group strongly supported by the polycyclic aromatic carbon sheets. The catalyst showed stability in its reusability for up to 6 cycles, hence a high potential stable and active bronsted heterogeneous acid catalyst.

Kefas et al., 2019 reported the esterification of PFAD using sulfonated D-glucose solid acid catalyst which was synthesized via modified sulfonation approach and was successfully utilized in a continuous oscillatory flow reactor to produce an environmentally friendly biodiesel under atmospheric conditions. Palm fatty acid distillate (PFAD) feedstock consisting of >90% free fatty acid was employed in a single step esterification reaction. The optimization of the process parameters conducted in the oscillation flow reactor (OFR) achieved >97% conversion of the PFAD to biodiesel with 94.21% FAME yield. The catalyst proved to be effective in the esterification reaction because of the availability of the high acid site density of the SO_3H groups and accessibility of methanol and PFAD mixture to the active acid sites. The results of the optimization of the process parameters showed that 6 Hz oscillation frequency (mixing rate) achieved 97.1% FAME (biodiesel) conversion. The optimum reaction time was 50 min with optimum molar ratio of 9:1 at optimum temperature of 60 °C confirming the effectiveness of the OFR technology in areas of mean residence time distribution, heat and mass transfer.

In general, due to high reaction temperatures and the need to avoid pretreatment step of FFA esterification to FAME before transesterification of triglycerides, an alternative use of heterogeneous catalysts for simultaneous esterification and transesterification reaction oils is being increasingly studied with the possibility of using them at mild reaction

temperatures. Besides, the cost of production of biodiesel can be reducing using these catalysts.

Heterogeneous Catalyst for Simultaneous Esterification and Transesterification Reaction

Low cost feedstocks with high FFA content react with alkali to form soap, causing serious emulsification and separation problems. In such feedstock with high FFA, biodiesel production became two-step catalytic process with first step involving esterification with an acid catalyst like sulfuric acid (feedstock pretreatment) to reduce FFA content and in a second step of transesterification of triglyceride using alkaline catalyst to produce biodiesel (Hayyan et al., 2010). However, the problem with the two-step method is catalyst separation from the biodiesel. Their presence in biodiesel product causes problem like for acid catalyst corrosion problem and alkaline catalyst incombustible ash problem, hence they are needed to be removed which will mean additional cost.

To avoid these situations, the bifunctional solid catalysts (heterogeneous catalysts) with both acidic and basic sites have been investigated which could simultaneously esterify FFA and transesterify triglycerides (TG) to biodiesel.

Bifunctional Solid Catalysts for Simultaneous Esterification and Transesterification Reaction

The recent bifunctional solid catalysts are discussed below as an alternative to the biodiesel production through simultaneous esterification and transesterification reaction as shown in Fig. 1. Table 1 highlighted bifunctional (acid-base) heterogeneous catalyst for simultaneous esterification and transesterification reactions operating at the optimum operating conditions for biodiesel production.

Farooq et al., 2013 studied bifunctional heterogeneous catalysts to develop an effective catalyst for the production biodiesel from waste cooking oil with improved catalytic activity and stability. The catalysts were prepared by using the modified impregnation method. Few drops of 0.01 M HNO_3 aqueous solution were added during impregnation to achieve the maximum adsorption of ions on the support. The results showed improved catalytic activity in the transesterification reaction of WCO at the reaction temperature of 100 °C for 4 h with methanol to oil molar ratio of 27:1 and an agitation speed of 500 rpm. Among the various catalysts tested, the Mo-Mn/g- Al_2O_3 -15 wt% MgO catalyst shows excellent catalytic with maximum yield of 91.4% biodiesel at the optimized reaction conditions. The improved catalytic activity is due to the presence of the optimum strength of the active sites on the surface of the Mo-Mn/g- Al_2O_3 -15 wt% MgO catalyst. Furthermore, the Mo-Mn/g- Al_2O_3 -15 wt% MgO catalyst showed substantial chemical stability and was reusable repeatedly for at least eight times for the production of biodiesel without significant loss in its catalytic activity. The study depicted that the synthesized bifunctional heterogeneous catalyst has the potential for biodiesel production from low cost feedstocks.

Borges et al., 2011 studied a natural porous silica (low cost) material, called pumice, as heterogeneous catalyst for the transesterification of sunflower oil and waste oil with methanol for biodiesel production. This porous material was subjected to ion exchange with a KOH aqueous solution to increase its activity. It proved to be an efficient heterogeneous particulate catalyst for the triglycerides transesterification and free fatty acids esterification from the feedstock at low temperature (55 °C). The high yield of

95.6 % obtained with waste oil as feedstock showed a bifunctional behavior of the catalytic material.

Jiménez-López et al., 2011 synthesized some zirconium doped MCM-41 silica supported WO_x solid acid catalysts by impregnation with ammonium met tungstate, with WO_3 loading ranging from 5 to 25 wt.%. The catalyst with 15 wt.% WO_3 loading showed maximum activity of 82 wt.% of FAME yield and was found to be able to simultaneously catalyze the esterification of FFA and transesterification of triglycerides present in a simulated used oil, with acidity of 9.1%. Besides, the catalyst retained its activity even in the presence of 5 wt.% of water and after three cycles of reuse, without any catalyst treatment.

Omar & Amin, 2011 performed transesterification of waste cooking palm oil to biodiesel over Sr/ZrO₂ catalyst. The amphoteric nature of zirconia, which contained basic and acid sites increased when strontium metal was doped on it. The basic and acid sites in the Sr/ZrO₂ enhanced the simultaneous transesterification and esterification reactions. Lee et al., 2015 developed a simple method for biodiesel production from high free fatty acid non-edible Jatropha oil using a bifunctional acid-base catalyst. The catalyst comprises of CaO and La₂O₃ mixed metal oxides, synthesized via co-precipitation method with various Ca/La atomic ratios. The co-precipitation of La with Ca promoted the CaO dispersion and this increased the surface acidic and basic sites instead of the bulk CaO and La₂O₃ metal oxide. The esterification and transesterification reaction of high FFA Jatropha oil was found to be enhanced as a result of the presence of acidity and basicity in the active sites of CaO- La₂O₃. The investigation of the effect of Ca/La atomic ratio ranging from 0.5 to 10.0 towards the transesterification activity among the series of CaO- La₂O₃ catalysts, showed 8.0 atomic ratios gave the highest biodiesel yield of 98.76% at conditions of 160°C reaction temperatures, 3 h, 25:1 methanol/oil molar ratio and 3 wt.% catalyst loading. However, the catalyst showed weak reusability in the first run reaction caused by the leaching of active Ca²⁺ and became stable for the next 4 cycles with reduced of Ca²⁺ ion leaching into the acid reaction medium. The leaching of the Ca²⁺ was as a result of partially soluble of free CaO that did not bind in the binary system leading to white layer Ca soap formation due to unfavorable neutralization of FFA with base Ca²⁺ species.

Alhassan et al., 2015 prepared ferric-manganese doped sulfated zirconia (FMSZ) nanoparticle solid acid catalyst through the impregnation reaction. This was followed by calcination at 600 °C for 3 h and characterization performed for synthesis of biodiesel using spent cooking vegetable oil with 17.5 % FFA. The FMSZ catalyst showed a higher surface area as compared to the zirconia sample and the dispersed Fe₂O₃ and MnO particles beside the sulfate group prevented the zirconia particles agglomerating resulting to an enhanced surface area, acidity and resultant significant biodiesel yield due its catalytic activity. Maximum yield of 96.5 ± 0.02% was achieved with catalyst being reused six times without loss in its activity under the optimized conditions: reaction temperature of 180 °C, 1:20 Molar ratio of oil to alcohol, stirring speed of 600 rpm and 3 wt/wt% catalysts loading. Also, a reduction of the free fatty acid content to 0.300 %, confirmed that the bi-functional FMSZ catalyst was very successful for simultaneous synthesis of the biodiesel.

Wei Liu et al., 2014 developed an efficient bifunctional catalyst organotriphosphonic acid-functionalized ferric alginate ATMP-FA. Researchers focused on the optimization of the catalytic performance in the esterification reaction of oleic acid for the production of biodiesel over the bifunctional catalyst. The reaction parameters include ethanol to oleic acid molar ratio, catalyst amount and reaction temperature have been optimized by response surface methodology (RSM) using the Box–Behnken model. Reaction temperature was found to be most significant factor, and the best conversion ratio of oleic acid reached 93.17% under reaction conditions of 9.53 wt% catalyst amounts and 8.62:1 of ethanol to oleic acid molar ratio at 91.0 °C. The catalyst showed excellent

catalytic property and reusability and two catalytic species could work cooperatively to promote the esterification reaction, making it a potential bifunctional catalyst for biodiesel production.

The SO₄²⁻/Zr-SBA-15 materials were synthesized and it showed an excellent catalytic activity in the transesterification of WCO with ethanol under optimized conditions. The triglyceride conversion and fatty acid methyl ester yields achieved was 98.5% and 95.2%, respectively with time = 3 h, molar ratio = 40, catalyst loading of 3 wt.% and temperature = 160 °C. More importantly, SO₄²⁻/Zr-SBA-15 materials displayed excellent stability and reusability, maintaining about 80% of triglyceride conversion after six reaction runs.

Table 1: Bifunctional (Acid-Base) Heterogeneous Catalyst for Simultaneous Esterification and Transesterification Reactions.

S/N	Catalyst	Feedstock	FFA (wt.%)	Optimum reaction Conditions	Biodiesel FAME yield	References
1	Mo-Mn/g-Al ₂ O ₃ -15 wt% MgO	Waste cooking oil	3.27a	T = 100 °C, t = 4 h Methanol/oil = 25:1 Catalyst amount= 3wt.%	91.4 %	(Farooq et al., 2013)
2	K-Pumice	Sunflower oil	0.17a	T = 55 °C, t = 2 h Methanol/oil = 18:1 Catalyst amount= 20wt.%	95.6%	(Borges, 2012)
3	WO ₃ /Zr-MCM-41	Sunflower oil	9.1	T = 115.5 °C, t = 2.5 h methanol/oil = 12:1 Catalyst amount=10 wt.%	79.7%	(Jiménez-López et al., 2011)
4	Sr/ZrO ₂	Waste cooking palm oil	5.08a	T = 115.5 °C, t = 87 min Methanol/oil = 29:1 Catalyst amount=2.7 wt.%	79.7%	(Omar & Amin, 2014)
5	CaO and La ₂ O ₃	Jatropha curcas oil	9.0	T = 160 °C, t = 3 h Methanol/oil = 25:1 Catalyst amount = 3 wt.%	98.76%	(Lee et al., 2015)
6	Fe ₂ O ₃ -MnO-SO ₄ ²⁻ /ZrO ₂	Waste cooking oil	17.5	T = 180 °C, t = 4 h Methanol/oil = 20:1 Catalyst amount = 3 wt.%	96.5%	(Alhassan et al., 2015)
7	ATMP-FA	Oleic acid		T = 91 °C, t = 10 h Ethanol/oil = 8.62:1 Catalyst amount=9.53 wt.%	93.17	(Wei Liu et al., 2014)
8	SO ₄ ²⁻ /Zr-SBA-15	Waste cooking oil	0.36a	T = 160 °C, t = 3 h Methanol/oil = 40:1 Catalyst amount = 3 wt.%	98.5% t 95.2%	(Yi et al., 2015)

a: Acid value (mg KOH/g) ; t: Triglyceride conversion

Heterogeneous Strong Acid Catalyst for Simultaneous Esterification and Transesterification Reactions

In recent decade there has been some advancement made possible in many industrial processes through the use of solid acid catalyst (Kaneda et al., 2006) and these advances is the presence of acidic sites on the surface of the solid acid catalysts which is in contrast to the definite acidic properties possessed by homogeneous acids (Morales et al., 2011). What makes the heterogeneous acid-catalyzed esterification distinct from the homogeneous catalysis is the interaction between the active sites of the catalyst and surface hydrophobicity (Trakarnpruk., 2012).

Discussed below are some heterogeneous solid acid catalysts also called strong solid acid catalyst that can simultaneously catalyze esterification and transesterification reactions (Leung et al., 2010) with high concentration of active sites (Iglesias et al, 2011). The use of such catalysts, which are efficient in both of these reactions, is preferable as most non-edible oil and waste cooking oil possesses high acid value that cannot undergo

alkaline transesterification without reduction in acid value. Besides, other advantages over common homogeneous catalysts like sulfuric is their easy removal, reusability and non-corrosiveness.

Rattanaphra et al., 2012 studied the simultaneous catalyzed transesterification of rapeseed oil and esterification of 10 wt% myristic acid with methanol using sulphated zirconia and without catalyst. The catalyst was prepared by solvent free method and a total of 86 % FAME was obtained at temperature of 170 °C, a catalyst loading of 3 wt%, molar ratio of oil to methanol of 1:20, pressure of 22 bar sand stirring rate of 600 rpm for 60 min. under these conditions, the FFA was observed to reach 2.95% (2.94 mg/ml sol). The rate of reaction was demonstrated to increase with each of these parameters within the ranges investigated. Generally, to achieve satisfactory biodiesel yield in simultaneous esterification and transesterification reactions using solid acid catalyst, harsh condition is required (e.g high temperature) because the reactions is slow. To achieve reasonable conversion under mild condition, a robust

catalyst is needful. Sulphated zirconia (a super solid acid catalyst) has been widely used for organic reactions (Eterigho et al., 2011) because it has strong acid sites obtained sulfur ions making it stable under thermal and hydrothermal conditions. In recent times chlorosulfuric acid was used as sulfating agent in the place of sulfuric acid to obtain a more robust sulfated catalyst (Yadav & Murkute, 2004).

The catalytic activities of $\text{HClSO}_3\text{-ZrO}_2$ were tested in simultaneous esterification and transesterification of rice bran oil. It was found to yield 100% FAME which is attributed to its diversity of acidity. Normally, activation of the carbonyl group of triglycerides is more difficult compared to that of FFA due to the presence of long alkyl chain in the bulky triglycerides molecules which increases the steric hindrances and interferences (Rattanaphra et al., 2010). The Zr-O-S bond formation and the elimination of HCl makes a more and stronger surface bond sulfate species leading to more effective carbonyl group activation. Crude rice bran oil usually requires a two-steps conversion or one step conversion with very harsh condition for simultaneous esterification and transesterification because of its high content (25–50%) of free fatty acid (FFA). Zhang et al., 2013 prepared chlorosulfonic acid modified zirconia ($\text{HClSO}_3\text{-ZrO}_2$) with strong acidity and it showed excellent catalytic activity toward simultaneous esterification and transesterification. The catalyst was able to convert simulated crude rice bran oil (refined oil with 40 wt% FFA) into biodiesel and the conversion yield stood at above 92% for at least three cycles, under a relative low reaction temperature of 120 °C, methanol/oleic acid molar ratio of 12:1, 6 wt% catalyst, and 12 h. Further investigation showed high activity maintained even with the presence of 40 wt% FFA and 3 wt% water. This shows that $\text{HClSO}_3\text{-ZrO}_2$ is a robust and durable catalyst indicating high potential to be commercial catalyst for biodiesel production from low grade feedstock.

Sulfated zirconia has been found to be a heterogeneous acid catalyst with very strong acidic sites (Zhao et al., 2008), in recent year researchers have supported it on alumina (Yee et al., 2011) and silica (Jiménez-López et al., 2011) achieving simultaneous esterification and transesterification reactions for vegetable oils with high FFA content as feedstock, under appropriate operating conditions.

Mesoporous sulfated Ti-SBA-15 (with Si/Ti ratio varying from 10 to 80) catalysts were synthesized and used for the preparation of biodiesel from unrefined canola oil (Sharma et al., 2014). It was found that the sulfation of Ti-SBA-15 increases the extent of transesterification by fourfold. Taguchi methodology was used to optimize the reaction parameters such as temperature, catalyst loading, methanol to oil molar ratio and reaction time towards methyl ester (biodiesel) formation through simultaneous esterification and trans-esterification reaction. Temperature and reaction time were found to be the most significant reaction parameters. In the study, 1 wt% catalyst yielded 91 wt% ester in 4 h when 15:1 methanol to oil molar ratio was used at 200°C. The catalyst was found to be reusable when studied up to 3 cycles.

Dawodu et al., 2014 reported a one-step catalytic conversion of non-edible seed oil, *Calophyllum inophyllum* with 15% free fatty acid into biodiesel over biomass-derived catalysts. In the study, an effective catalyst that was prepared by sulphonation of carbon materials with

concentrated H_2SO_4 was able to catalyze oil with 15% free fatty acid into biodiesel. Carbon material carbonized for 1 h had smaller carbon sheets which were able to bind more atoms resulting in higher SO_3H and total acid densities than the catalyst derived from material carbonized for 5 h. At the optimized conditions of temperature 180 °C, reaction time 5 h, methanol to oil of 30:1, and catalyst concentration of 5 wt.%, 99.0% conversion of the vegetable oil to FAME was achieved. Overall, Cat-1 showed superior transesterification activity over Cat-2 but was more susceptible to leaching due to the smaller carbon sheets formed during carbonization. Utilization of these catalysts could reduce biodiesel cost associated with the water-washing step in homogeneous catalyzed reaction.

Carbohydrate-derived catalysts were prepared by Lou et al. 2008 from various carbohydrates namely D-glucose, sucrose, cellulose and starch. The textural properties and catalytic of the prepared catalysts were investigated in detail. The result revealed that the starch-derived catalyst had the best catalytic performance. The carbohydrate-derived catalysts showed higher catalytic activities for both esterification and transesterification compared to sulphated zirconia and Niobic acid solid, and gave an enhanced yield of methyl esters in converting 27.8 wt% high free fatty acids (FFAs) content waste cooking oils to biodiesel. The preparation of the carbohydrate catalysts by incomplete carbonization and sulfonation with sulfuric acid produces a sulfo-polycyclic aromatic hydrocarbon with robust structure, highly stable and hydrophobic during reaction. Also, the large amount of SO_3H presence increases the activities of the catalysts making them stable under acidic or basic conditions. These sugar derived catalyst showed higher esterification and transesterification activities than sulphated zirconia and niobic acids due the higher acid sites densities (4-6 times larger) even though the typical solid acid catalyst have much larger surface area. Furthermore, the starch-derived catalyst retained a remarkably high yield of about 93% of its original catalytic activity even after 50 cycles of successive re-use under the optimized reaction conditions. Thus the solid acid catalyst displayed very excellent operational stability. Clearly, the results indicate that the carbohydrate-derived catalysts, especially the starch-derived catalyst, are highly effective, recyclable, eco-friendly and promising solid acid catalysts that are highly suitable for biodiesel production from waste oils containing high free fatty acids.

Heterogeneous Biocatalyst for Transesterification in Biodiesel Production

Biocatalysts are catalyst obtained from living organism. Examples of such catalyst are extracellular lipase that obtained from microbial broth and intracellular lipase obtained inside cell or cell wall. Use of biocatalyst can reduce the unwanted by-product (soap and pigment), application of low temperature and its stable during biodiesel production unlike other heterogeneous catalyst (Marina et al., 2021; Pandit et al., 2023). Despite the significance in using biocatalyst in biodiesel production there is some drawbacks which include difficulty in separation and purification processes and is not cheap. (Faruque et al., 2020; Mardhiah et al., 2017) in their review papers reported that use of biocatalyst in biodiesel production increase the yield of the product but the only thing to the catalyst is highly sensitive to water and it may be reduce the catalytic activity of the enzymes..

Heterogeneous Nanocatalysts for Transesterification in Biodiesel Production

This is a new progress of catalyst in biodiesel production. The catalysts are known to improve the rate of transesterification reaction by removing unwanted processes and unnecessary reactions. Another advantage of the catalysts is simple to recover it after biodiesel production, reusability, and cost-effectiveness. In addition, the catalysts enduring high FFA and moisture content, essential in certain insensitive high temperature and pressure (Pandit et al., 2023). The cost-effective heterogeneous catalysts help out to diminish the overall cost of biodiesel production. These catalysts may be made to have a maximum yield of a reaction product by altering the number of atoms, surface functionality, and elemental composition, and they also have an efficient surface area, high stability, and higher resistance to saponification. There are variety of techniques, including vacuum deposition, self-propagating high-temperature synthesis, evaporation, coprecipitation, electrochemical deposition, microwave combustion, hydrothermal, solvothermal, impregnation, and sol-gel technology. These catalysts are formed from nanoparticles with less than 100 nm variety of sizes and morphologies. They demonstrate critical advantages for both heterogeneous and homogeneous catalysts in terms of activity, selectivity, efficiency, and reusability. Here, biodiesel nanocatalysts are divided into magnetic, nonmagnetic and carbon types. (Alemu & Alemu, 2023).

Magnetic Nanocatalysts

Magnetic nanocatalysts can be obtained from selected materials, such as metal oxides, iron, cobalt, nickel, and platinum alloys, which can be applied in various ways. Magnetic nanoparticles (MNPs) have several favorable characteristics: higher molecular weight and smaller size (thus, a good ratio of surface area to volume); quantum characteristics; and capacity to transport other chemicals (such as drugs). These catalysts can be used in biofuel industries, like in the synthesis of sugars using lignocellulosic stuff by using immobilized enzymes, or used to attach other catalytic nanoparticles, making them ideal nanoparticle for use in several applications. Another advantage of using 'MNPs-enzymes' is the possibility of collecting the enzyme complex using magnetic field, and reusing it more than once. By using a high-frequency magnetic field, these nanocatalysts may also be utilized for hydrogenation, photooxidation, and inductive heating. Magnetic nanoparticles also act as carriers for enzymes, which will be more manageable in a magnetic field range (Pandit et al., 2023). Examples of magnetic catalysts used to make biodiesel are Fe_3O_4 , $\text{CaO}/\text{Fe}_3\text{O}_4$, $\text{Ca}(\text{OH})_2/\text{Fe}_3\text{O}_4$, $\text{Cs}/\text{Al}/\text{Fe}_3\text{O}_4$, $\text{KF}/\text{CaO}-\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{MgO}/\text{MgFe}_2\text{O}_4$, and $\text{Ca}/\text{Fe}_3\text{O}_4/\text{SiO}_2$. Alemu & Alemu, 2023 in their review paper reported the use of the $\text{CaO}-\text{Fe}_3\text{O}_4$ magnetic catalyst in the generation of biodiesel from palm seed oil. Also cadmium oxide and tin oxide magnetic nanocatalysts have been utilized for esterification, transesterification, and hydrolysis reactions of soybean oil. Furthermore, more active catalysts Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (MNPs) have been used as fundamental recyclable catalysts achieving 96% yield production. The catalyst $\text{ZnO}/\text{BiFeO}_3$ was also a promising catalyst for the generation of biodiesel from canola oil and yields of 95.43 and 95.02% in the first and second cycles, respectively. Another example, SnO produces 84% yield of esterification without loss, at

200°C after 1 h reaction. Therefore, magnetic catalyst shows fast, clean, superior stability, and recyclability. (Alemu & Alemu, 2023)..

Nonmagnetic Nanocatalysts

The ability to reuse the catalysts allows for lower-cost biodiesel production in a fixed-bed reactor. There are number of nonmagnetic nanocatalysts, such as hydrotalcite, metal oxides, sulfated oxides, zeolites, and zirconia, which are frequently employed in the manufacture of biodiesel. Molina, 2013 also used ZnO nanorods to produce biodiesel from olive oil and realized that their catalytic performance yield of 94.8% was slightly higher than the regular ZnO yield of 91.4%. Borah et al 2018 reported a maximum production of 98.03% at a methanol/oil ratio of 9 at 60°C for 3 hours with 2.5 wt% Co/ZnO catalysts for biodiesel. Zhang et al. 2020 improved by using the surface modification of the $\text{NaAlO}_2/c-\text{Al}_2\text{O}_3$ with the M/O of 20.79:1, 10.89 wt% catalysts, and at 64.72°C to achieve the highest biodiesel production, which was 97.65%. Alkaline earth metal compounds, in particular, Ca-enclose nanomaterials, have the potential to be nonmagnetic catalysts for the transesterification of biodiesel. The most widely used nonmagnetic catalysts include MgO/TiO_2 , $\text{Mg}-\text{Al}$ hydrotalcite, KF/CaO , Mg/Al , Li/CaO MgO , metal-organic frameworks (MOFs), Nanozeolites, potassium-doped zeolite, and hydrotalcite. The implementation of nanocatalysts gets much attention due to vast surface area strong catalytic performance, and appropriate charge transport channel (Alemu & Alemu, 2023).

Carbon Nanocatalysts

Nanocatalysts are created from carbon materials, including grapheme, carbon nanotubes and reduced graphene oxides. Due to their diverse structural, mechanical, thermal, and biocompatibility qualities, carbon nanocatalysts are good catalysts and have advantageous applications in electrocatalytic devices such as fuel cells and other electro-processing systems. Carbon nanotubes (CNTs) are often manufactured from graphite sheets that have been wound into cylinder forms. They have a large surface area, measured in nanometers, and are incredibly biocompatible (Bano et al., 2020; Pandit et al., 2023). Ibrahim et al. 2020 developed nanocatalyst ($\text{Na}_2\text{O}/\text{CNT}$) using impregnation method for the production of biodiesel using used cooking oil as feedstock under the condition of catalyst amount (3wt%), methanol to oil ratio of 20:1, reaction time (3h) and reaction temperature (66°C). The biodiesel yield obtained was 97% with the catalyst recyclability of 3 times. In conclusions using nanocatalyst in biodiesel production can have better conversion of fatty acids because of greater surface area and different functional group as reported (Bano et al., 2020).

Conclusion

Several types of heterogeneous catalysts have been developed and used for the production of biodiesel namely basic, acidic and acid-base catalysts. The heterogeneous basic catalysts have shown to be effective for low FFA feedstocks producing high yield and conversion of biodiesel. However, they have limitation of being sensitive to high FFA feedstocks and water content of feedstocks as well as possible soap formation. In this case, oils will need to be pretreated to reduce its FFA content. Heterogeneous acid-base (bifunctional) and strong acids catalysts are potential catalyst for biodiesel production due to they can catalyze both esterification and transesterification reactions

simultaneously. Solid catalysts with the presence of acid and base catalytic sites proves to be the best for biodiesel production because they allow production process to be in a single step and will avoid the problem arising from the use homogeneous catalyst. Furthermore, the use of nanomaterial and agricultural waste have shown to improved catalyst properties also the addition of transition metals in the preparation of catalyst have been reported to generate new active site which can enhance the catalyst performance and biodiesel production (Kefas et al., 2024).

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