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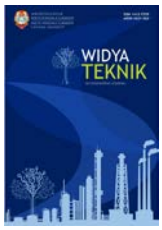

Review Article

A Review of the Development and Role of Heterogeneous Catalysts for Biodiesel Production

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Abstract: Indonesian regulations regarding the implementation of B30 encourage a significant increase in biodiesel demand. Moreover, this implementation will continue to be increased to B35 in 2025 and is projected to reach B100 in 2045. This high demand for biodiesel needs to be supported by the development of adequate biodiesel production technology where the catalyst is one aspect that plays an important role in biodiesel production. The use of catalysts aims to accelerate biodiesel production so that high biodiesel yields and good quality are achieved. In biodiesel production, the choice of catalyst greatly influences the operating conditions, the products produced, the subsequent purification process, and the environmental impacts. Moreover, the changing trend in biodiesel raw materials from food to non-food ingredients requires the development of catalysts that are more suitable for the raw materials used in biodiesel production. The specific characteristics of each catalyst play an important role in the transesterification reaction to produce biodiesel where this needs to be supported and adapted to optimum operating conditions, especially in terms of alcohol-to-oil molar ratio, catalyst amount, temperature, pressure, and reaction time. This review provides a comprehensive overview of the various heterogeneous catalysts used to assist the transesterification reactions in biodiesel production.

Keywords: biodiesel; catalyst; heterogeneous; transesterification

1. Introduction

Biodiesel is a renewable energy that is being developed rapidly, especially in developing countries like Indonesia. Regarding Indonesia's success in implementing B30 regulations, the Organization for Economic Co-operation Development (OECD) in collaboration with the Food and Agriculture Organization (FAO) of the United Nations (UN) reported that consumption of vegetable oil-based biodiesel in Indonesia is predicted to continue increasing to 23% in the period 2021–2030 (OECD/FAO, 2021). Currently, the raw materials for biodiesel mostly come from vegetable oils, such as palm oil (Crabbe et al., 2001), soybean oil (Han et al., 2005), sunflower oil (Pimentel and Patzek, 2005), and coconut oil (Jitputti et al., 2006). Competition in the use of vegetable oils in the food and energy sectors results in uncontrolled prices and supply chains so it often leads to deforestation in several tropical countries due to the opening of new plantations. In 2021, the Indonesian Ministry of Trade and the Indonesian Ministry of Agriculture also reported an increase in the price of agricultural products compared to the previous year (Timorria, 2021). This causes a shift in the choice of raw materials, from food to non-food.

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Catalysts play an important role in biodiesel production, especially with changes in current raw material trends. Homogeneous base catalysts, such as potassium hydroxide and sodium methylate, are more widely used for mass production of biodiesel compared to homogeneous acid catalysts (sulfuric acid, hydrochloric acid, and phosphoric acid). This is because a homogeneous base catalyst can provide a higher reaction rate and yield, and requires a lower alcohol-to-oil ratio (Fattah et al., 2020; Kaur and Ali, 2011; Kouzu and Hidaka, 2012). However, biodiesel production using a homogeneous base catalyst also requires complicated steps for purifying the final product, such as acid washing and centrifugation (Santosa et al., 2019; Suryaputra et al., 2013). Therefore, the use of homogeneous catalysts is generally limited to high-quality raw materials. The use of non-food raw materials which have lower quality certainly requires special treatment. High water and free fatty acid contents increase the formation of soap which results in the biodiesel production process being inefficient (Yuliana et al., 2020).

On the other hand, heterogeneous catalysts offer various advantages compared to homogeneous catalysts because these catalysts are insensitive to impurities in the raw material, can be reused, and are easily separated from the reaction products (Suryaputra et al., 2013). Previous studies have reported the synthesis of biodiesel using heterogeneous acid or base catalysts, such as base-modified zirconium (Omar and Amin, 2011), polyoxometalate-based sulfonated ionic liquid immobilized on the surface of the UiO-66-2COOH metal-organic framework (Xie and Wan, 2019), modified Amberlyst-15 (Boz et al., 2015), sulfonic acid-modified carbon nanotubes (Liu et al., 2016), sulfated niobium oxide (da Conceição et al., 2016), superacid solid catalyst (SO_4^{2+}/ZrO_2-TiO_2/La^{3+}) (Y. Li et al., 2010), and modified mesoporous silica (Rahadi et al., 2021; Suryajaya et al., 2021). In this review, various types of catalysts used in biodiesel production are discussed and each catalyst has its characteristics and advantages.

2. Heterogeneous base catalysts

2.1. Alkali and alkaline earth metal-based catalysts

Alkali metal oxides are the most widely exploited base catalysts in the transesterification process. The surface structure of calcium oxide (CaO), one of the alkali metal oxides, can be seen in Figure 1. Zhang et al., 1988 demonstrated the alkaline properties of metal oxides using carbon dioxide sorption analysis where the adsorbed carbon dioxide was analyzed for its desorption capacity using temperature-programmed desorption (TPD). Due to their high basicity and low price, metal oxides are the most widely studied and used for heterogeneous catalysts in biodiesel production. One of the most commonly used metal oxides is CaO which offers various advantages, such as long catalyst life, high catalytic activity under moderate reaction conditions, and low solubility in methanol (Latchubugata et al., 2018; Roschat et al., 2016). Arun et al., 2017 studied biodiesel production from *Terminalia belerica* and *Garcinia gummi-gutta* using CaO catalyst under these transesterification conditions: temperature of 60°C, reaction time of 3 hours, catalyst amount of 2% (w/v), and methanol-to-oil molar ratio of 9:1. Before it was used, the CaO catalyst was dried in an oven at 125°C for 12 hours and then calcined at 605°C for 5 hours.

Roschat et al. (2016) converted olein from palm oil with a free fatty acid (FFA) content of 0.29 mg KOH/g using a limestone-based CaO catalyst. This catalyst was synthesized by drying it at 100°C for 24 hours and then crushed, sieved, and calcined at 800°C. A biodiesel yield of 97.20% was obtained using this CaO catalyst. A reusability study shows that this CaO catalyst could be used 5 times without a significant decrease in activity (biodiesel yield > 90%).

Apart from CaO, oxides of alkaline earth metals are also widely used in biodiesel production. Du et al., 2019 synthesized three types of composites composed of magnesium oxide (MgO) and carbon-based organic materials using a combination of sol-gel and calcination techniques, namely MgO-polyvinyl acetate (PVA), MgO-urea, and MgO-ethylene glycol (GLY), where these three catalysts were used to produce biodiesel from castor oil. The transesterification reaction was carried out with an ethanol-to-oil molar ratio of 12:1 and a catalyst amount of 6% (w/w) at 75°C. The greatest conversion (96.5%) was obtained by MgO-urea calcined at 800°C and followed by MgO-PVA and MgO-GLY with conversions of 93.6% and 91.8%, respectively.

Meanwhile, Manríquez-Ramírez et al., 2013 studied the catalytic activity of MgO impregnated with potassium hydroxide (KOH), sodium hydroxide (NaOH), and cerium oxide (CeO_2). The basicity levels of these three catalysts are as follows: MgO-KOH > MgO-NaOH > MgO-CeO_2. Based on the study, the biodiesel yield obtained by these three catalysts respectively was >99, 78, and 56% under these reaction conditions: temperature of 60°C, reaction time of 1 hour, and methanol-to-oil mass ratio of 4:1.

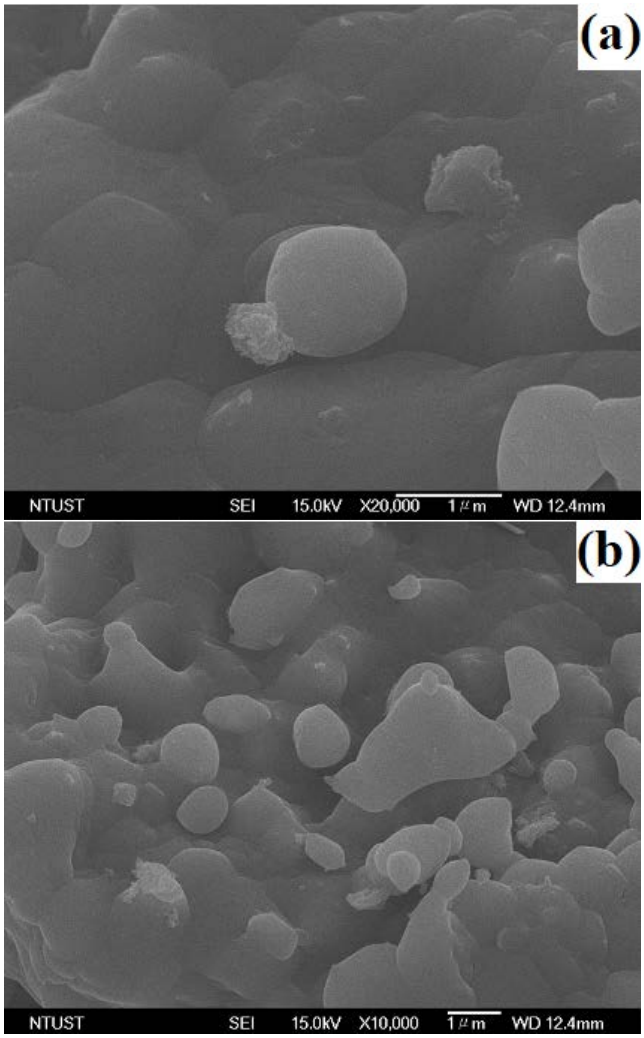

Figure 1. The surface structure of CaO based on scanning electron microscopy (SEM) analysis with a magnification of (a) 20,000 times and (b) 10,000 times

Roschat et al., 2018 studied palm oil-based biodiesel production using a strontium oxide (SrO) catalyst through an ethanolysis reaction. Optimum reaction conditions were obtained with an ethanol-to-oil molar ratio of 12:1 and a catalyst amount of 5% (w/w) at 80°C for 3 hours where the biodiesel yield reached 98.2%. This SrO catalyst can also be reused five times while maintaining a biodiesel yield above 90%. The use of SrO catalyst in biodiesel production was also carried out by Liu et al., 2007. This study examined the use of SrO catalyst in the transesterification of soybean oil into biodiesel. The results showed that the biodiesel yield (<95%) was obtained at below 70°C within 30 minutes. The reusability of SrO catalyst is quite high as can be seen from its ability to maintain continuous activity in 10 cycles.

Mootabadi et al., 2010 carried out the transesterification of palm oil with ultrasonic assistance using three different types of alkaline earth metal-based catalysts, namely CaO, SrO, and barium oxide (BaO). Based on the study, BaO and SrO catalysts produced the highest biodiesel yield (95.2%), followed by CaO (77.3%) within 1 hour. The fabrication of a lithium-based catalyst, namely lithium–iron oxide ($LiFe_5O_8$-$LiFeO_2$), through mixing iron(III) oxide (Fe_2O_3) and lithium carbonate (Li_2CO_3) solution was studied by Dai et al., 2018. The solid resulting from the precipitation reaction is then calcined at 800°C to obtain the $LiFe_5O_8$-$LiFeO_2$ catalyst. Using this catalyst, the yield of soybean oil-based biodiesel was 96.5% under these operating conditions: temperature of 65°C, reaction time of 2 hours, methanol-to-oil molar ratio of 36:1, and catalyst amount of 8% (w/w). This catalyst can be used up to 5 times with a biodiesel yield of above 94%.

2.2. Supported alkali and alkaline earth metal-based catalysts

Boron group-based compounds, especially alumina (Al_2O_3), are very often used as supports for various metal oxides, metal halides, and metal nitrates (Chouhan and Sarma, 2011). Kesserwan et al., 2020 reported a CaO/Al_2O_3 hybrid aerogel used to catalyze the methanolysis reaction of used cooking oil. This catalyst was prepared by a fast sol-gel method initiated by epoxide and followed by a calcination process at 700°C under supercritical carbon dioxide conditions. This study reported that the biodiesel yield (89.9%) can be achieved under these optimum conditions: methanol-to-oil molar ratio of 11:1, catalyst amount of 1% (w/w) with a CaO/Al_2O_3 molar ratio of 3:1, temperature of 65°C, and reaction time of 4 hours. Benjapornkulaphong et al., 2009 also studied the synthesis process of various alkali and alkaline earth metal nitrates supported by Al_2O_3, such as $LiNO_3$/Al_2O_3, $NaNO_3$/Al_2O_3, $Ca(NO_3)_2$/Al_2O_3, KNO_3/Al_2O_3, and

$Mg(NO_3)_2/Al_2O_3$ via impregnation method and followed by calcination at 450-850°C. These catalysts were used for the transesterification reaction of palm kernel oil and coconut oil. Here, the calcination temperature significantly affects the biodiesel yield. $Ca(NO_3)_2/Al_2O_3$ and $LiNO_3/Al_2O_3$ catalysts provided biodiesel yields of up to 90% when calcined at 450°C. However, a higher calcination temperature reduces the yield to <5%. This study recommends using a $Ca(NO_3)_2/Al_2O_3$ catalyst amount of 10% (w/w) and 15-20% (w/w) for the transesterification of palm kernel oil and coconut oil, respectively. The optimum reaction condition was obtained with a methanol-to-oil molar ratio of 65:1 at 60°C for 3 hours.

2.3. Base organocatalysts

Cerro-Alarcón et al., 2010 used gem-diamine which has neighboring nitrogen atoms as a base organocatalyst in the transesterification of sunflower oil using a methanol-to-oil molar ratio of 10:1. This study also found that intrinsic alkalinity is not the only factor controlling catalyst activity in the biodiesel production but sufficient steric ability to abstract and re-release protons are also required for efficient transesterification.

Apart from gem-diamine, base organocatalysts could also be obtained through impregnation of tetramethylguanidine (Faria et al., 2008) or 3-(N,N'-dicyclohexylguanidine)-propyltrimethoxysilane (Balbino et al., 2011) onto the surface of silica gel. The catalytic activity of both catalysts in the transesterification of soybean oil for biodiesel production gave yields of around 87% and 98%, respectively, after 3 hours. The catalyst can be reused several times with similar catalytic activity. Guanidine bases, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene, have also been used for the functionalization of SBA-15 where this composite was then used as a biodiesel catalyst (Meloni et al., 2011). During the reaction time, leaching of the catalyst occurred only at a very low rate. This allows the reuse of the catalyst after regeneration through a simple treatment using NaOH. During the treatment, the catalyst base sites bound by free fatty acids can be freed so that the catalytic activity can be restored.

In transesterification reactions, quaternary ammonium salts also showed high activity even in the immobilized state. Despite their low basicity, mesoporous molecular sieves from the M41S family containing organic templates, such as [CTA]Si-MCM-48, [CTA]Si-MCM-50, and [CTA]Si-MCM-41, were good catalysts for transesterification of rapeseed oil with a methanol-to-oil molar ratio of 18:1 at moderate temperature (79°C) (Fabiano et al., 2010). However, comparative studies used 3-(trimethylammonium)-propyl functionalized on silica gel chloride (QN^+Cl^-/SiO_2) and silica gel hydroxide (QN^+OH^-/SiO_2) as well as styrene-divinylbenzene polymer functionalized with $-CH_2N(CH_3)^{3+}$ indicate that the quaternary ammonium salt bound to silica will be removed during the reaction through leaching (Y. Liu et al., 2007). Leaching of the active sites of the QN^+OH^-/SiO_2 catalyst occurs through breaking the alpha bond on the methylene part to the ammonium center. Leaching of quaternary ammonium ions can also occur as a result of nucleophilic attack of hydroxy and/or methoxy ions on the alpha carbon, leaving only the tertiary amine behind. Other deactivation routes also consider the presence of weak acidity on the silanol groups on the silica surface and the nucleophilic attack of the Si-O groups on the methylene groups attached to the ammonium ion. Meanwhile, for styrene-divinylbenzene polymer, this leaching does not occur much under the same reaction conditions.

Another example of an immobilized quaternary ammonium salt is phosphanezium. Kim et al., 2009 studied the impregnation of phosphazenium hydroxide into silica which showed high activity in the transesterification of tributyrin with excess methanol. This organocatalyst can be used repeatedly without experiencing significant deactivation. Meanwhile, Zafiropoulos et al., 2007 reported that poly/divinyl benzene/n-phenyl-4-vinylaniline, a diarylammonium derivative catalyst, could be used to catalyze the esterification of free fatty acids into methyl esters where the free fatty acid content was reduced from 12-40% to 0.5-1% (w/w).

2.4. Mixed metal oxide-based catalysts

Mixed metal oxides are widely used as base catalysts where the basicity level can be adjusted by changing the chemical composition and synthesis procedures (Teo et al., 2017). The type of synthesis method, activation temperature, and raw material structure have a significant influence on the basicity level of these mixed metal oxides (Mckenzie et al., 1992; Tichit et al.,

1995). Salinas et al., 2018 studied the catalytic activity of a composite between zirconium oxide (ZrO_2) and 1-5% (w/w) lanthanum oxide (La_2O_3) which was synthesized using the sol-gel method and then calcined at 600°C. The combination of these two metal oxides increases catalytic activity by modifying their acid-base properties. La_2O_3 impregnated into ZrO_2 formed a monoclinic-ZrO_2 structure and increased its basicity level which plays a key role in the catalysis process. This study stated that the addition of 3% (w/w) La_2O_3 to ZrO_2 was the optimum percentage for transesterification of canola oil into biodiesel.

Limmanee et al., 2013 studied the catalytic activity of combined metal oxide nanocrystals as a heterogeneous catalyst, namely calcium/magnesium/zinc (Ca/Mg/Zn) oxide. This Ca/Mg/Zn oxide was made by the coprecipitation method using sodium carbonate (Na_2CO_3) as a precipitator and then used in the synthesis of palm kernel oil biodiesel through methanolysis. In the conversion of palm kernel oil into biodiesel via methanolysis, this study reported a maximum biodiesel yield of 97.5% (w/w) using Ca/Mg/Zn oxide nanocrystals fabricated using Ca/Mg/Zn molar ratio of 3:1:1, Na_2CO_3 concentration of 0.75 mol/L, and $Ca/Mg(CO_3)_2$-to-$Ca/Zn(CO_3)_2$ ratio of 1:1. The reaction conditions used were methanol-to-oil molar ratio of 20:1, catalyst amount of 6% (w/w), and temperature of 60°C.

Santiago-Torres et al., 2014 studied the use of sodium zirconate (Na_2ZrO_3) as a basic catalyst for transesterification of soybean oil. This study reported a maximum biodiesel conversion of 98.3% (w/w) within 3 hours at 65°C using a catalyst amount of 3% (w/w). Meanwhile, Lee et al., 2015 synthesized a bifunctional acid-base catalyst consisting of metal oxides, namely CaO and La_2O_3, through a co-precipitation process. The integration of the two materials increases the catalytic activity due to the dispersion of CaO on the composite surface which increases the surface acid and base sites compared to the individual metal oxides. This study reported that the highest biodiesel yield (98.76%) was obtained with a methanol-to-oil molar ratio of 25:1 and a catalyst amount of 3% (w/w) at 160°C for 3 hours.

2.5. Transition metal-based catalysts

Titanium oxide (TiO_2) and zinc oxide (ZnO) are among the transition metal oxides used as heterogeneous base catalysts for biodiesel production (Yoo et al., 2010). Kaur et al., 2018 reported the use of a TiO_2/SiO_2 composite catalyst combined with tungsten using the sol-gel method in the transesterification of cottonseed oil waste to produce biodiesel. The optimum transesterification reaction was achieved within 4 hours with an methanol-to-oil molar ratio of 30:1 and a catalyst amount of 5% (w/w) at 65°C. This study reported that this catalyst can be used up to 4 times without significant reduction in catalytic activity. Meanwhile, Madhuvilakku and Piraman, 2013 studied the catalytic activity of a mixture of titanium and zinc oxide (TiO_2-ZnO) for the palm oil transesterification process. The yield of biodiesel produced reached 92% by adding 200 mg TiO_2-ZnO under the following reaction conditions: methanol-to-oil molar ratio of 6:1, temperature of 60°C, and reaction time of 5 hours. This study also reported a better yield compared to the single oxide catalyst, such as ZnO (83%).

2.6. Hydrotalcite-based catalysts

Hydrotalcite is a classification of alkaline anionic clay with the general formula $Mg_6Al_2CO_3(OH)_{16}.4H_2O$. Hydrotalcite is widely used as a heterogeneous base catalyst because (1) its adjustable high basicity level by changing the Mg/Al molar ratio and (2) better catalyst morphology compared to alkaline earth metal oxides. However, non-homogeneity and sensitivity to impurities, such as FFA and water, are major disadvantages for this type of catalyst. Navajas et al., 2018 studied the catalytic activity of hydrotalcite synthesized with a Mg/Al molar ratio of 1.5-5 by co-precipitation in the transesterification reaction of sunflower oil. This study reported an optimum conversion of 96% under these conditions: methanol-to-oil molar ratio of 48:1, pressure of 1 atm, temperature of 60°C, catalyst amount of 2% (w/w), and reaction time of 24 hours. This study linked the catalytic activity to the presence of Brønsted base sites present on the crystal surface.

Nowicki et al., 2016 studied the catalytic performance of hydrotalcite impregnated with zirconium (Zr) to process rapeseed oil into biodiesel. This study found that the tetravalent Zr cation (Zr^{4+}) was very effective in significantly increasing the catalytic activity of the catalyst. An optimum conversion of 99.9% was reported using hydrotalcite with a Zr/Mg/Al molar ratio of 0.45:2.55:1 at 373–393 K and 4.8-5.0 atm for 6 hours.

Trakarnpruk and Porntangjitlikit, 2008 studied the catalytic activity of a hydrotalcite composite with an Mg/Al molar ratio of 4:1 and potassium in the transesterification of palm oil with methanol. This study reported a methyl ester yield of 86.6% with the following reaction parameters: methanol-to-oil molar ratio of 30:1, temperature of 100°C, reaction time of 6 hours, and catalyst amount of 7% (w/w). Zeng et al., 2009 also studied that immobilization of the lipase enzyme from *Saccharomyces cerevisiae* on hydrotalcite with an Mg/Al molar ratio of 4:1 via an adsorption technique could significantly increase enzyme performance. Transesterification of rapeseed oil carried out with immobilized lipase which could produce a biodiesel yield of 96% within 4.5 hours using a catalyst amount of 1.5% (w/w) at 45°C and atmospheric pressure. This biocatalyst-hydrotalcite composite can maintain high activity with a conversion reaching 81.3% after 10 reuse cycles.

2.7. Waste-based catalysts

Calcium-rich solid waste originating from industrial processes and the surrounding environment can be developed as a solid base catalyst that is cheap, sustainable, and environmentally friendly (Majhi and Ray, 2016; Pandit and Fulekar, 2017). Shells of clams, eggs, clams, snails, and oysters; fish scales; animal bones; and ash originating from plant species are calcium-rich solid wastes that are easily obtained at low prices (Marwaha et al., 2018). Calcium obtained from various wastes can be converted into CaO, the most widely used heterogeneous base catalyst, through the calcination method. Yaşar, 2019 studied the catalytic activity of eggshell-based CaO and compared it with pure CaO for the conversion of rapeseed oil into biodiesel. The maximum biodiesel yield obtained using pure CaO and eggshell-based CaO was 96.81 and 95.12% under the following transesterification conditions: methanol-to-oil molar ratio of 9:1, catalyst amount of 4% (w/w), temperature of 60°C, and reaction time of 1 hour.

Sirisomboonchai et al., 2015 reported the catalytic activity of calcined clam shells in the transesterification of used cooking oil using methanol. A biodiesel yield of 86% was obtained through transesterification using a catalyst amount of 5% (w/w) and a methanol-to-oil molar ratio of 6:1 at 65°C for 2 hours. The same catalyst can be used for up to four conversion cycles with a 20% reduction in yield from the first cycle due to the formation of calcium glyceroxide on the catalyst surface.

Hu et al., 2011 synthesized a catalyst derived from freshwater mussel shell waste in the transesterification of animal fats. This catalyst was synthesized using three steps, namely calcination, impregnation, and activation. These freshwater mussel shells were initially calcined at 900°C, impregnated in water, and then activated by calcination at 600°C for 3 hours. A biodiesel yield of >90% was obtained through a transesterification reaction with a methanol-to-oil molar ratio of 12:1 and a catalyst amount of 5% (w/w) at 70°C for 1.5 hours. The catalyst also demonstrated excellent reuse rates with yield reductions of only 10-15% found after 12 conversion cycles.

2.8. Superbase catalysts

The use of superbase catalysts in the conversion of oil and fat into biodiesel allows the reaction time to be reduced to a shorter length. Bota et al., 2010 studied that a superbase catalyst produced from the thermal decomposition of mesoporous γ-alumina (γ-Al_2O_3)-supported sodium azide (NaN_3) (or called NaN_3/MSU-g 84) showed high efficiency in the transesterification of soybean oil with methanol in a batch reactor. A yield of 60% was achieved under these reaction conditions: temperature of 60°C, reaction time of 2 hours, stirring speed of 300 rpm, catalyst amount of 1 gram, and methanol-to-oil molar ratio of 9:1. The NaN_3/MSU-g 84 superbase catalyst also showed high catalytic ability where a conversion of 60% can be achieved in just 15 minutes with increasing the methanol-and-oil molar ratio to 27:1 (Bota et al., 2010). Another study on the manufacture of a Na/NaOH/γ-Al_2O_3 heterogeneous catalyst through treatment of γ-Al_2O_3 with sodium hydroxide and sodium metal at 320°C under nitrogen also showed that this catalyst was capable of producing a 94% yield of soybean oil-based biodiesel under the following conditions: temperature of 60°C, reaction time of 2 hours, and methanol-to-oil molar ratio of 9:1 (Kim et al., 2004). This reaction was carried out using the solvent n-hexane with a n-hexane-to-oil molar ratio of 5:1.

3. Heterogeneous acid catalysts

3.1. Heteropoly acid-based catalysts

Heteropoly acids (HPA) and their salts are often used as solid heterogeneous acid catalysts in the biodiesel production process (Alcañiz-Monge et al., 2018; Hanif et al., 2017). HPA which has a Keggin structure is preferred and widely used because it has high thermal stability and can be synthesized easily compared to other types of HPA. However, Keggin-type HPA has a low specific surface area so it needs to be supported using appropriate supports. Supported HPA can be used in biodiesel production due to its structural mobility and super acidity. Kurhade and Dalai, 2018 studied 12-tungstophosphoric acid (TPA) ($H_3PW_{12}O_{40}.nH_2O$) impregnated on a γ-Al_2O_3 catalyst for biodiesel production. An optimal conversion of 94.9 ± 2.3% was achieved with a catalyst amount of 10% (w/w) and a methanol-to-oil molar ratio of 17.5:1 at 200°C and 4 MPa within 10 hours. A conversion of 90.3 ± 4.3% was achieved in the second cycle of catalyst reuse. Siddiquee et al., 2011 also studied the catalytic activity of structured mesopore silica (SBA-15) impregnated with HPA for the production of biodiesel from fats in waste sludge. A biodiesel yield of 30.14% (w/w) was obtained with an HPA concentration in the system of 15% at 135°C and 135 psi for 3 hours.

3.2. Sulfonic acid-based catalysts

Sulfonic acid-based catalysts are generally formed from polymers, especially polystyrene, which are cross-linked with sulfonic acid, and have the advantage of being non-corrosive and environmentally friendly (Mansir et al., 2017). This type of catalyst has high catalytic activity due to the attraction between fatty acids and alcohol hydroxyl groups dispersed in the polymer. In addition, sulfonic acid groups attached to the polymer chain also increase the acidity level of the active site of the catalyst (Vaccari, 1999). Some examples of sulfonic acid-based catalysts are non-porous Nafion resin and porous Amberlyst resin. Kiss et al., 2006, López et al., 2007, and López et al., 2005 stated that these two catalysts showed high initial activity and then dropped drastically after 2-4.5 hours of use in the reaction, making them unsuitable for use in industry.

Silica-supported Nafion resin (SAC-13) emerged as a more promising catalyst in sunflower oil methanolysis and palmitic acid esterification using a methanol-to-palmitic acid molar ratio of 18.5:1 at 60°C. This catalyst composite does not require activation so it is advantageous in terms of preparation (Ni and Meunier, 2007). Deactivation of the SAC-13 catalyst by water can also be easily overcome by mixing a new SAC-13 catalyst or by drying the catalyst using dry gas. This study also observed the high stability of SAC-13 catalytic activity as measured by batch reactors and fixed bed reactors with recirculation systems. It is considered that it can be used in a wide range of applications.

Liu et al., 2008 studied the synthesis of functionalized mesoporous carbon using sulfonic acid. This heterogeneous acid catalyst was then used in the esterification process of oleic acid with ethanol at 80°C under N_2 atmosphere conditions in a closed flask. The research results showed that this catalyst is very efficient due to its high acid content and hydrophobic surface properties. Meanwhile, Andrijanto et al., 2012 studied a sulfonic acid catalyst impregnated on the surface of hyper-crosslinked polystyrene (D5082) for the esterification of oleic acid with methanol. The results showed that D5082 has high catalytic activity even though it has a low number of acid sites and acidity levels. This study attributed the high catalytic activity of D5082 to the accessibility of the acid sites and its good dispersion across the surface of the catalyst particles.

Caetano et al., 2009 and Granados et al., 2011 also reported various types of polymers cross-linked with sulfonic acids, such as (1) polyvinyl alcohol cross-linked with sulfosuccinic acid and poly(styrenesulfonic acid) and (2) polystyrene cross-linked with divinylbenzene and sulfonic acid groups. Compared with Amberlyst or Nafion, the catalytic activity of the sulfonic acid functionalized polymer showed good conversion and stability in the esterification of palmitic acid with methanol and ethanol at low temperatures (60-80°C) where only 5% of the sulfosuccinic acid was removed from the catalyst surface after seven reaction cycles. However, this catalyst also required a very high alcohol-to-fatty acid ratio of more than 30:1. In the animal fat transesterification process, the catalyst activity is also relatively low, only producing a conversion of around 60% after 90 hours. Guerreiro et al., 2006 also reported similar results where a polyvinyl alcohol membrane cross-linked with

sulfosuccinic acid was used as an acid catalyst in the transesterification process of soybean oil at 60°C with a very high amount of excess methanol.

3.3. Sulfonic acid-based catalysts

Sulfated metal oxides are generally used as acid heterogeneous catalysts in esterification reactions (Chen et al., 2007; Shi et al., 2016). Kaur and Ali, 2015 studied the effectiveness and reusability of Ce/ZrO_2-TiO_2/SO_4^{2-} in catalyzing the esterification reaction of oleic acid with methanol or ethanol. The activity of the Ce/ZrO_2-TiO_2/SO_4^{2-} catalyst depended on the concentration of Brønsted acid sites contributed by cerium. The catalyst with 2% (w/w) cerium calcined at 600°C showed the highest catalytic activity. With a catalyst amount of 5% (w/w) and a methanol-to-oil molar ratio of 6:1, 98% conversion can be achieved in the vegetable oil esterification process at 65°C for 1 hour. This study also reported no significant decrease in activity up to five reaction cycles.

Ropero-Vega et al., 2010 studied the catalytic activity of titania sulfated with ammonium sulfate [TiO_2/SO_4^{2-}-$(NH_4)_2SO_4$] and sulfuric acid (TiO_2/SO_4^{2-}-H_2SO_4). This study found that sulfated catalysts have a high level of acidity. FTIR analysis showed the presence of Lewis and Brønsted acid sites for the TiO_2/SO_4^{2-}-$(NH_4)_2SO_4$ catalyst and only Lewis acid sites for the TiO_2/SO_4^{2-}-H_2SO_4 catalyst. Further analysis showed very high activity for the esterification of oleic acid with ethanol where a conversion of 82.2% could be achieved after 3 hours at 80°C. Meanwhile, de Almeida et al., 2008 reported the use of sulfated titania (TiO_2/SO_4^{2-}) for methanolysis of soybean oil and castor oil at 120°C with a methanol-to-oil molar ratio of 6:1. A biodiesel yields of 40% and 25%, respectively, were obtained during 60 minutes of reaction.

The catalytic activity of carbon-supported sulfated polyaniline was also studied by Zięba et al., 2010 in the transesterification of triglycerides (triacetin and castor oil) and esterification of ricinoleic fatty acid with methanol at 50-60°C. The activity of this catalyst was not very good because it required a very high methanol-to-oil molar ratio in the reaction process. Deposition of the polymer on carbon support also causes a decrease in catalytic activity because some of the active sites interact with the support. However, these catalysts have almost the same activity in the reuse cycle.

3.4. Sulfonic acid-based catalysts

Lewis acid-modified catalyst with raw materials based on silica ($SiO_2/ZnCl_2$; $SiO_2/FeSO_4$), alumina ($Al_2O_3/ZnCl_2$; $Al_2O_3/FeSO_4$), niobium ($Nb_2O_5/ZnCl_2$; $Nb_2O_5/FeSO_4$), and charcoal (charcoal/$ZnCl_2$; charcoal/$FeSO_4$) can be used to catalyze esterification reactions using microwaves (Barbosa et al., 2006). As a Lewis acid metal, niobium can also be impregnated on other catalyst materials (silica), one example is mesoporous niobium silicate. This material was prepared through two procedures, namely (1) impregnation of MCM-41 silica with niobium oxalate followed by calcination and (2) structural incorporation of niobium into MCM-41 silica during the synthesis process (García-Sancho et al., 2011). Its catalytic activity was evaluated in the transesterification reaction of sunflower oil with methanol where the catalyst performed well at rather high reaction temperatures and excess methanol-to-oil molar ratios.

Amino acid complexes with zinc [ZnL_2] can be an effective catalyst for the conversion of oils with high levels of free fatty acids in vegetable oils (Kolaczkowski et al., 2009). Its impregnation into a support in the form of cordierite with monolithic crystallinity allowed it to be used in fixed bed conditions. Its use in the transesterification of rapeseed oil with a methanol-to-oil molar ratio of 12:1 using a continuous tube reactor produced a moderate yield. However, the study stated that the MgO component in cordierite which has the structure $2MgO.2Al_2O_3.5SiO_2$ can be a contributor to the catalytic activity in this research, especially at high temperature (195°C) and pressure (20 bar).

Tantalum oxide (Ta_2O_5) is a solid Lewis acid catalyst that can be deposited on silica and has high acid activity when the tantalum content reaches 15% (w/w) (Pârvulescu et al., 2007). The study conducted by Jiménez-Morales et al., 2011 also obtained similar results where the catalytic activity of the Ta_2O_5 and SBA-15 composite with a tantalum content of 15% (w/w). A maximum biodiesel yield (92.5%) was obtained in the methanolysis of sunflower oil at 200°C with a methanol-to-oil molar ratio of 12:1.

Sodium molybdate (Na_2MoO_4) has also been investigated as a heterogeneous catalyst for methanolysis of soybean oil. Molybdenum(VI) complexes exhibit high Lewis acidity and bind to hydroxyl bonds in alcohols forming transition

components that have high nucleophilic properties (Nakagaki et al., 2008). The transesterification reaction using this catalyst requires low temperature, short time, and normal pressure. This catalyst can also be easily regenerated and reused after the washing process.

Iron metal and zinc cyanide complexes can also act as solid catalysts in making biodiesel from vegetable oils (Sreeprasanth et al., 2006). This catalyst is hydrophobic and contains only Lewis acid sites. Coordinated Zn^{2+} ions that do not fully interact with other components in the iron-zinc cyanide complex structure are designated as active sites. This complex shows high activity for the transesterification of triglycerides and esterification of free fatty acids present in crude cooking oil and used waste oil, as well as other low-quality oils.

3.5. Sulfonic acid-based catalysts

Sulfated zirconia is often used in the esterification of fatty acids with various alcohols ranging from 2-ethylhexanol to methanol. A study showed that the reaction rate catalyzed by sulfated zirconia was three times higher than the reaction without a catalyst (Kiss et al., 2006). Zirconia tungstate catalysts were also reported to exhibit superacidic properties (Hino and Arata, 1988). This catalyst could achieve high effectiveness when paired with the right solvent. Ngaosuwan et al., 2010 studied the esterification reaction of lauric acid carried out at 130°C and 12.2 atm using a zirconia tungstate catalyst with hexane co-solvent. Its high catalytic activity can be attributed to the non-polarity and low kinematic viscosity of this hexane co-solvent. In contrast, tetrahydrofuran (THF) which has a higher polarity tends to reduce the catalytic activity of zirconia tungstate because THF competes to interact with the active sites on the catalyst surface and is also involved in side reactions with methanol.

López et al., 2007b reported that the esterification and transesterification rates increased with increasing tungsten oxide (WO_x) density up to 6.6 atom/nm^2 and then decreased for densities above 6.6 atom/nm^2. The growth of tungsten trioxide (WO_3) crystal species results in lower esterification and transesterification rates which is consistent with a decrease in the number of active sites.

Comparative studies of tungstate zirconia and sulfated zirconia with amorphous titania-zirconia composites in the tricapryline transesterification and caprylic acid esterification processes showed that sulfated zirconia was more active, while tungstate zirconia was the most stable and could be recycled (López et al., 2008). However, research by Pârvulescu et al., 2007 also showed that sulfated zirconia is also an easily deactivated material due to the presence of water and chemically bound molecules (Omota et al., 2003). In addition, this sulfated zirconia catalyst can also lose some sulfur during the reaction, making it difficult to recycle and reuse. Meanwhile, titania-zirconia composites were found to have greater activity for transesterification than zirconia tungstate because the basic sites on zirconia tungstate can interact with carboxylic acids during esterification and degrade their active sites during the catalysis process.

Lanzafame et al., 2011 compared the catalytic activity of zirconia and sulfated zirconia impregnated onto the surface of SBA-15 with H_2SO_4 and Amberlyst-15 in the etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol. The activity of each of these catalysts is closely related to its structural characteristics. The yield of products, such as 5-(ethoxymethyl)furan-2-carbaldehyde (EMF) and ethyl-4-oxopentanoate (EOP), is influenced by the presence of Lewis and/or Bronsted acid sites on the catalyst, while the formation of 1,1-dietoxyethane (DE) as one of the by-products is related to imperfect active sites. Figure 2 shows the HMF etherification reaction network to form valeric ester which is a component of biodiesel. The study conducted by W. Li et al., 2010 suggested the use of three-dimensional (3D) mesoporous sulfated zirconia supported by organosilica and bridged by ethane in the esterification and transesterification reaction processes because of its higher activity and stability compared to sulfated zirconia. Combining organosilica-ethane with a sulfated zirconia catalyst results in good catalyst mesoporosity and increased hydrophobic properties which can significantly increase the transesterification activity. In addition, through fabricating this composite, the sulfate groups in the catalyst will not easily decompose during the reaction so the catalyst can maintain its activity for up to three reaction cycles.

Incorporating zirconium in SBA-15 using zirconocene dichloride as a metal precursor (Zr-SBA-15) can be an alternative method for loading zirconium with high concentrations and still maintaining good mesoscopic regularity. The Zr-

SBA-15 catalyst showed an acidity level that was strong enough to provide high catalytic activity in the transesterification of crude palm oil with methanol for biodiesel synthesis. Yields of more than 70% could be achieved in batch reactors at 200°C using a methanol-to-oil molar ratio of 30:1 (Iglesias et al., 2011). The impregnation of titanium, molybdenum, and tungsten as doping metals on this catalyst only provided a slight increase in the acidity of Zr-SBA-15.

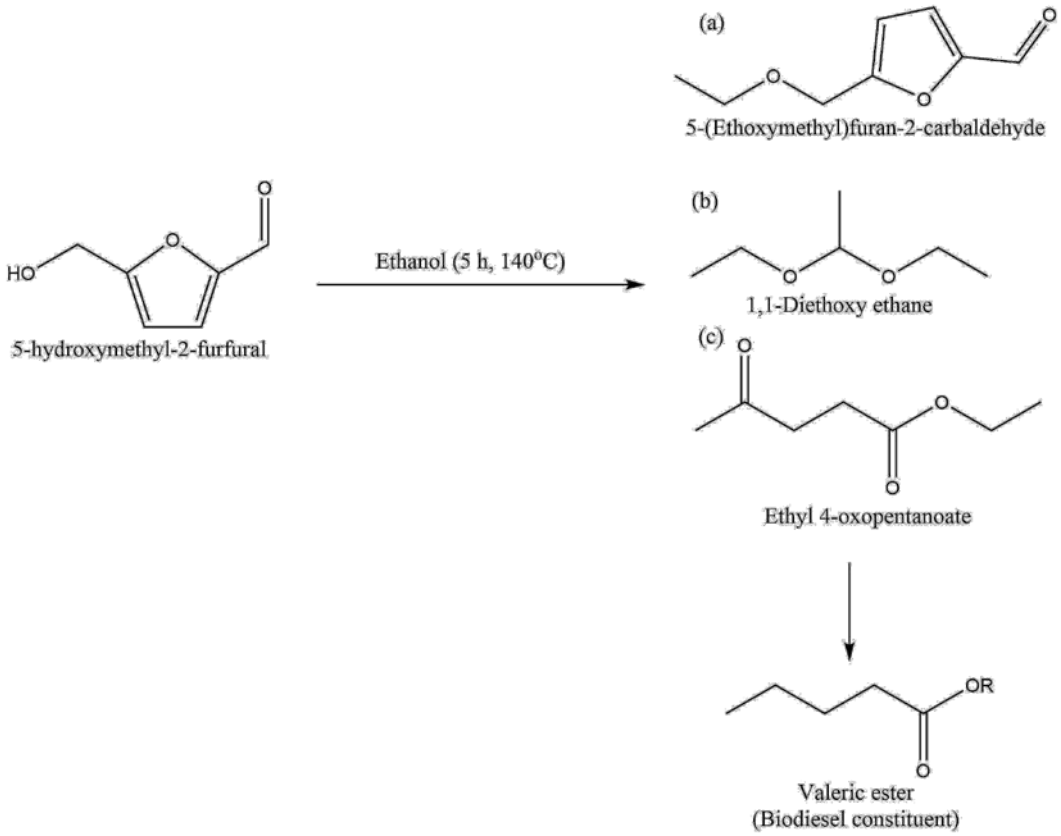

Figure 2. Scheme of the etherification reaction of 5-hydroxymethyl-2-furfural (HMF) with ethanol using a mesopore silica catalyst (Lanzafame et al., 2011)

Jiménez-Morales et al., 2010 reported that WO_3 deposition on zirconia-MCM-41 composite was able to induce esterification of oleic acid with a high methanol-to-oil molar ratio at 65°C, resulting in a moderate biodiesel yield. This activity was achieved with WO_3 loading ranging from 5-25% (w/w), although the amount of tungsten that interacts with the silica support to achieve this activity was not explained.

4. Heterogeneous acid-base (bifunctional) catalysts

As discussed previously, oils with a high free fatty acid content require an acid catalyst to esterify the free fatty acid content before transesterification with a base can take place. Therefore, catalysts with acid and base sites that are capable of carrying out esterification and transesterification simultaneously with minimum soap formation are very interesting to develop (Semwal et al., 2011). This type of catalyst generally has a Lewis acid site which plays a role in the esterification reaction of carboxylic acids with methanol and a conjugated base site which catalyzes the transesterification reaction of triglycerides with methanol. Depending on the type of reactants and reaction parameters, this type of catalyst can work as an acid catalyst, base catalyst, or bifunctional catalyst.

Metal-organic frameworks (MOFs) are emerging as attractive and versatile porous crystalline materials in the field of heterogeneous catalysis, owing to their extremely high internal surface area, tunable porosity, diverse chemical structures, good thermal stability, and modular synthetic design (Valvekens et al., 2013). Exposed metal sites (or so-called coordinative unsaturated metal centers) in MOF structures

are known to act as adsorption sites and Lewis acids and can play a central role in inducing catalytic activity and selectivity for various reactions. Several types of MOFs that have been investigated for biodiesel production include iron and copper benzenetricarboxylates (Fe-BTC and Cu-BTC), MIL-53(Fe), UiO-66, and Cr(III) and Co(II) terephthalate (Marso et al., 2020; Nikseresht et al., 2017; Pangestu et al., 2019; Zhang et al., 2020). These MOF catalysts are capable of producing biodiesel with high yields (85-95%) from oleic acid (Nikseresht et al., 2017; Zhang et al., 2020) through one esterification step or two esterification and transesterification steps (Marso et al., 2020). Lunardi et al., 2021 studied the use of the $Zn_3(BTC)_2$ catalyst which has a triclinic crystal structure in the synthesis of biodiesel from low-quality palm oil. The maximum yield of biodiesel (89.9%) was obtained at 65°C for 4.5 hours using a methanol-to-oil ratio of 6:1 and a catalyst amount of 1% (w/w). The biodiesel obtained had characteristics that comply with ASTM D6751 and SNI 7182-2015.

Meanwhile, Suryajaya et al., 2021 and Rahadi et al., 2021 studied the catalytic activity of hollow and double-shelled silica-based catalysts. The inner shell of this catalyst is synthesized by adding ammonia as a base site, while the outer shell is impregnated with iron (II) and copper (II) metals as Lewis acid sites, respectively. This catalyst can work with two functions, namely acid and base catalysts. The yield of biodiesel produced by these two catalysts was 85.36% and 87.14%, respectively. The operating conditions used were using a methanol-to-oil mass ratio of 5.3:1 to 6:1 and a catalyst amount of 5-6% (w/w) at 55.3-60°C for 4.5-5 hours. These two catalysts have the ability to recycle up to 4 times with similar biodiesel yields.

5. Ion exchange resins

5.1. Cation exchange resins

Cation exchange resins have long been used for pre-esterification of free fatty acids contained in vegetable oils, especially with low molecular weight alcohols (de Rezende et al., 2008; Jeromin et al., 1987; Kiss et al., 2006; Liu et al., 2008; Marchetti and Errazu, 2008; Pasias et al., 2006; Tesser et al., 2005; Yadav and Thathagar, 2002). The reaction was carried out at low temperatures (60-80°C) but a high methanol-to-fatty acids molar ratio of 1:1 to 20:1 was required to achieve high conversion. Generally, sulfonated resins are classified into two types based on differences in their matrix structure: gelular and macro-reticular (Kouzu et al., 2011). For the gelular type, the degree of cross-linking of the styrene-divinylbenzene copolymer formed in the resin matrix is lower compared to the macro-reticular copolymer. Gelular resins are more suitable for acid-catalyzed reactions that occur in polar liquid phases because low cross-linking is effective in swelling the resin matrix in polar components such as methanol. On the other hand, although the macro-reticular type has a lower swelling ability than the gelular type, the diffusion of nonpolar components is faster in macro-reticular resin because of its many wide pores. A comparison of the two types of resin has been carried out in the pre-esterification of free fatty acids with methanol (Kouzu et al., 2011). The gelular type resin was found to be superior in catalytic activity compared to the macro-reticular type. This is caused by the large number of catalytic acid sites found in the gelular type. However, internal mass transfer is faster in macro-reticular type resins. Russbueldt and Hoelderich, 2009 concluded that the gelular type resin has advantages because of its greater swelling ability in methanol compared to the macro-reticular type. Meanwhile, for macroporous resins, the reaction should occur only at superficial sulfonic acid groups on the surface, not inside the pores.

Fu et al., 2015 reported the catalytic activity of sulfonated macro-reticular polystyrene-divinyl benzene (ST-DVBSO_3H) resin in the esterification of FFA with a high acid value (64.9 mg KOH/g). The maximum FFA conversion of 97.8% was achieved when the reaction was carried out under the following conditions: catalyst amount of 10% (w/w), methanol-to-oil molar ratio of 15:1, temperature of 100°C, and reaction time of 3 hours. Feng et al., 2011 also studied the continuous esterification of used cooking oil with an acid value of 36.0 mg KOH/g in a fixed bed reactor using commercial cation exchange resin (NKC-9). This study reported a conversion rate of 98% over 500 hours of reaction at 65°C with a methanol-to-oleic acid mass ratio of 2.8:1, catalyst height in the fixed bed of 44.0 cm, and feed flow rate of 0.62 mL/min.

The transesterification reaction with methanol on a cation exchange catalyst also depends on the polarity of the fatty acid chain in the ester. Research conducted using Dowex DR2030 sulfonate resin as a heterogeneous

catalyst shows that apart from steric hindrance, the polarity of the fatty acid chain in the ester influences the reaction rate (Alonso et al., 2009). The effect of polarity, whether positive or negative, is caused by the repulsive or attractive interactions of the ester chains with the polar groups of the resin and/or with the methanol molecules present in the pores. A very positive effect occurs when hydrogen bonds can stabilize intermediate components that participate in determining the reaction rate. The presence of polar groups in the ester chain increases the reaction rate, and conversely. If the polar groups do not show this capacity, the reaction rate is almost unaffected.

5.2. Cation exchange resins

Anion exchange resin can be used as a heterogeneous base catalyst in the transesterification reaction of triolein and low molecular weight alcohols. Acid cation exchange resins also show positive results in the esterification of oils containing high levels of free fatty acids with methanol. Acid-functionalized anion exchange resins also showed stability. For example, Purolite CT-275 was able to maintain its stability under batch conditions in eight batches. Another advantage is that there is no need for washing after use (Pasias et al., 2006), making it attractive to use.

6. Immobilized enzyme catalysts

The biodiesel preparation route via chemical catalysis requires quite high energy and produces undesirable side products, namely soap and polymer-based pigments, which inhibit the separation of products from glycerol, di- and monoacylglycerol (Gog et al., 2012). Biocatalysts or enzyme-based catalysts are widely studied because they can remove obstacles. Two types of enzymatic biocatalysts that are generally used in biodiesel production are extracellular lipase and intracellular lipase. Extracellular lipase is an enzyme that has been taken from the broth of microorganisms and then purified. On the other hand, intracellular lipase is found in the cell-producing walls or inside the cells. The main producing microorganisms for extracellular lipase are *Rhizopus oryzae*, *Mucor miehei*, *Candida antarctica*, and *Pseudomonas cepacian* (Amini et al., 2017a, 2017b).

In contrast to chemical catalysts, biocatalysts also work as a source of triglycerides, with FFA ranging from 0.5 to 80% (Aransiola et al., 2014). The advantages of enzymatic biodiesel production include easy product separation, moderate processing temperatures (35-45°C), no by-products, and reusable catalysts (Christopher et al., 2014; Mardhiah et al., 2017). However, the disadvantage of using extracellular enzymes as catalysts is the complexity of the catalyst purification procedure, as well as the costs required. This weakness can be overcome by using lipase-producing microbial cells as biocatalysts, such as filamentous fungi. However, the lipase used in whole-cell form cannot be reused at the end of the reaction. Another method to overcome this weakness is to immobilize the enzyme into a solid matrix. Several reports indicated that buffered lipases are good catalysts for biodiesel production from vegetable oils and waste oils (Soumanou and Bornscheuer, 2003; Watanabe et al., 2001, 2000). Nassreddine et al., 2008 reported the use of commercial lipase from *Candida antarctica* (Lipozyme) encapsulated using silica aerogel and supported by silica quartz fibers in the methanolysis of biodiesel from sunflower seed oil. A conversion of 90% was obtained with a methanol-to-oil molar ratio of 3:1 at 40°C for 50 hours. Similar results were also obtained in the ethanolysis of soybean oil with commercial immobilized lipase type B from *Candida antarctica* (Rosset et al., 2011) where a biodiesel yield of 87% was obtained at 32°C for 24 hours. Ethyl ester production by enzymatic ethanolysis is also not sensitive to the addition of water up to 4.0% (v/v) of alcohol. This increases the opportunity to be able to use ethanol with fairly high water content in the transesterification reaction catalyzed by lipase. Regeneration of lipase from immobilized *Candida antarctica* for transesterification has also been reported (Chen and Wu, 2003).

Several commercial immobilized lipases that are widely studied are Novozym 435, Lipozyme TL IM, Lipozyme RM IM, and Lipase PS-C (Gog et al., 2012). In its use, important parameters that influence the yield of biodiesel for enzymatic synthesis are lipase type, substrate type, substrate concentration, pH, temperature, and distance between enzyme molecules and substrate

7. Conclusion

Various types of catalysts have been investigated to support and accelerate biodiesel production. Each type of catalyst has its own specific characteristics which are suitable for certain processes in biodiesel production. Nowadays, the biodiesel industries have many options for catalysts that can be matched with their processes, raw materials, operating conditions, catalyst reusability, and environmental aspects. In the future, catalyst research can continue to be developed to obtain high biodiesel yields at low cost and low environmental impact, considering the increasing need for biodiesel with the implementation of B30 regulations in Indonesia.

Author contributions

Conceptualization – M.Y., S.I., F.E.S; data analysis – M.Y., C.J., C.G., A.A.A.; resources – M.Y., S.P.S., J.N.P., S.L.; writing original draft – M.Y., C.J.

Conflict of interest

The authors declare no conflict of interest.

References

Alcañiz-Monge, J., Bakkali, B. El, Trautwein, G., Reinoso, S., 2018. Zirconia-supported tungstophosphoric heteropolyacid as heterogeneous acid catalyst for biodiesel production. Appl Catal B 224, 194–203. https://doi.org/10.1016/j.apcatb.2017.10.066

Alonso, D.M., Granados, M.L., Mariscal, R., Douhal, A., 2009. Polarity of the acid chain of esters and transesterification activity of acid catalysts. J Catal 262, 18–26. https://doi.org/10.1016/j.jcat.2008.11.026

Amini, Z., Ilham, Z., Ong, H.C., Mazaheri, H., Chen, W.H., 2017a. State of the art and prospective of lipase-catalyzed transesterification reaction for biodiesel production. Energy Convers Manag 141, 339–353. https://doi.org/10.1016/j.enconman.2016.09.049

Amini, Z., Ong, H.C., Harrison, M.D., Kusumo, F., Mazaheri, H., Ilham, Z., 2017b. Biodiesel production by lipase-catalyzed transesterification of Ocimum basilicum L. (sweet basil) seed oil. Energy Convers Manag 132, 82–90. https://doi.org/10.1016/j.enconman.2016.11.017

Andrijanto, E., Dawson, E.A., Brown, D.R., 2012. Hypercrosslinked polystyrene sulphonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis. Appl Catal B 115–116, 261–268. https://doi.org/10.1016/j.apcatb.2011.12.040

Aransiola, E.F., Ojumu, T. V., Oyekola, O.O., Madzimbamuto, T.F., Ikhu-Omoregbe, D.I.O., 2014. A review of current technology for biodiesel production: State of the art. Biomass Bioenergy 61, 276–297. https://doi.org/10.1016/j.biombioe.2013.11.014

Arun, S.B., Suresh, R., Yatish, K. V., Omkaresh, B.R., Channa Keshava Naik, N., 2017. Use of CaO and Na3PO4 Catalysts in the Synthesis of Biodiesel and Investigation of Fuel Properties. Mater Today Proc 4, 11111–11117. https://doi.org/10.1016/j.matpr.2017.08.074

Balbino, J.M., De Menezes, E.W., Benvenutti, E. V., Cataluña, R., Ebeling, G., Dupont, J., 2011. Silica-supported guanidine catalyst for continuous flow biodiesel production. Green Chemistry 13, 3111–3116. https://doi.org/10.1039/c1gc15727b

Barbosa, S.L., Dabdoub, M.J., Hurtado, G.R., Klein, S.I., Baroni, A.C.M., Cunha, C., 2006. Solvent free esterification reactions using Lewis acids in solid phase catalysis. Appl Catal A Gen 313, 146–150. https://doi.org/10.1016/j.apcata.2006.07.015

Benjapornkulaphong, S., Ngamcharussrivichai, C., Bunyakiat, K., 2009. Al2O3-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil. Chemical Engineering Journal 145, 468–474. https://doi.org/10.1016/j.cej.2008.04.036

Bota, R.M., Houthoofd, K., Grobet, P.J., Jacobs, P.A., Leuven, K.U., 2010. Superbase catalysts from thermally decomposed sodium azide supported on mesoporous γ-alumina. Catal Today 152, 99–103. https://doi.org/10.1016/j.cattod.2010.01.002

Boz, N., Degirmenbasi, N., Kalyon, D.M., 2015. Esterification and transesterification of waste cooking oil over Amberlyst 15 and modified Amberlyst 15 catalysts. Appl Catal B 165, 723–730. https://doi.org/10.1016/j.apcatb.2014.10.079

Caetano, C.S., Guerreiro, L., Fonseca, I.M., Ramos, A.M., Vital, J., Castanheiro, J.E., 2009. Esterification of fatty acids to biodiesel over polymers with sulfonic acid groups. Appl Catal A Gen 359, 41–46. https://doi.org/10.1016/j.apcata.2009.02.028

Cerro-Alarcón, M., Corma, A., Iborra, S., Martínez, C., Sabater, M.J., 2010. Methanolysis of sunflower oil using gem-diamines as active organocatalysts for biodiesel production. Appl Catal A Gen 382, 36–42. https://doi.org/10.1016/j.apcata.2010.04.024

Chen, J.-W., Wu, W.-T., 2003. Regeneration of immobilized Candida antarctica lipase for transesterification. J Biosci Bioeng 95, 466–469.

Chen, X.R., Ju, Y.H., Mou, C.Y., 2007. Direct synthesis of mesoporous sulfated silica-zirconia catalysts with high catalytic activity for biodiesel via esterification. Journal of Physical Chemistry C 111, 18731–18737. https://doi.org/10.1021/jp0749221

Chouhan, A.P.S., Sarma, A.K., 2011. Modern heterogeneous catalysts for biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews 15, 4378–4399. https://doi.org/10.1016/j.rser.2011.07.112

Christopher, L.P., Hemanathan Kumar, Zambare, V.P., 2014. Enzymatic biodiesel: Challenges and opportunities. Appl Energy 119, 497–520. https://doi.org/10.1016/j.apenergy.2014.01.017

Crabbe, E., Nolasco-Hipolito, C., Kobayashi, G., Sonomoto, K., Ishizaki, A., 2001. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. Process Biochemistry 37, 65–71.

da Conceição, L.R. V., Carneiro, L.M., Rivaldi, J.D., de Castro, H.F., 2016. Solid acid as catalyst for biodiesel production via simultaneous esterification and transesterification of macaw palm oil. Ind Crops Prod 89, 416–424. https://doi.org/10.1016/j.indcrop.2016.05.044

Dai, Y.M., Wang, Y.F., Chen, C.C., 2018. Synthesis and characterization of magnetic LiFe5O8-LiFeO2 as a solid basic catalyst for biodiesel production. Catal Commun 106, 20–24. https://doi.org/10.1016/j.catcom.2017.12.002

de Almeida, R.M., Noda, L.K., Gonçalves, N.S., Meneghetti, S.M.P., Meneghetti, M.R., 2008. Transesterification reaction of vegetable oils, using superacid sulfated TiO2-base catalysts. Appl Catal A Gen 347, 100–105. https://doi.org/10.1016/j.apcata.2008.06.006

de Rezende, S.M., de Castro Reis, M., Reid, M.G., Lúcio Silva, P., Coutinho, F.M.B., da Silva San Gil, R.A., Lachter, E.R., 2008. Transesterification of vegetable oils promoted by poly(styrene-divinylbenzene) and poly(divinylbenzene). Appl Catal A Gen 349, 198–203. https://doi.org/10.1016/j.apcata.2008.07.030

Du, L., Li, Z., Ding, S., Chen, C., Qu, S., Yi, W., Lu, J., Ding, J., 2019. Synthesis and characterization of carbon-based MgO catalysts for biodiesel production from castor oil. Fuel 258. https://doi.org/10.1016/j.fuel.2019.116122

Fabiano, D.P., Hamad, B., Cardoso, D., Essayem, N., 2010. On the understanding of the remarkable activity of template-containing mesoporous molecular sieves in the transesterification of rapeseed oil with ethanol. J Catal 276, 190–196. https://doi.org/10.1016/j.jcat.2010.09.015

Faria, E.A., Ramalho, H.F., Marques, J.S., Suarez, P.A.Z., Prado, A.G.S., 2008. Tetramethylguanidine covalently bonded onto silica gel surface as an efficient and reusable catalyst for transesterification of vegetable oil. Appl Catal A Gen 338, 72–78. https://doi.org/10.1016/j.apcata.2007.12.021

Fattah, I.M.R., Ong, H.C., Mahlia, T.M.I., Mofijur, M., Silitonga, A.S., Rahman, S.M.A., Ahmad, A., 2020. State of the art of catalysts for biodiesel production. Front Energy Res 8. https://doi.org/10.3389/fenrg.2020.00101

Feng, Y., Zhang, A., Li, J., He, B., 2011. A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. Bioresour Technol 102, 3607–3609. https://doi.org/10.1016/j.biortech.2010.10.115

Fu, J., Chen, L., Lv, P., Yang, L., Yuan, Z., 2015. Free fatty acids esterification for biodiesel production using self-synthesized macroporous cation exchange resin as solid acid catalyst. Fuel 154, 1–8. https://doi.org/10.1016/j.fuel.2015.03.048

García-Sancho, C., Moreno-Tost, R., Mérida-Robles, J.M., Santamaría-González, J., Jiménez-López, A., Maireles-Torres, P., 2011. Niobium-containing MCM-41 silica catalysts for biodiesel production. Appl Catal B 108–109, 161–167. https://doi.org/10.1016/j.apcatb.2011.08.025

Gog, A., Roman, M., Toşa, M., Paizs, C., Irimie, F.D., 2012. Biodiesel production using enzymatic transesterification - Current state and perspectives. Renew Energy 39, 10–16. https://doi.org/10.1016/j.renene.2011.08.007

Granados, M.L., Alba-Rubio, A.C., Sádaba, I., Mariscal, R., Mateos-Aparicio, I., Heras, Á., 2011. Poly(styrenesulphonic) acid: An active and reusable acid catalyst soluble in polar solvents. Green Chemistry 13, 3203–3212. https://doi.org/10.1039/c1gc15461c

Guerreiro, L., Castanheiro, J.E., Fonseca, I.M., Martin-Aranda, R.M., Ramos, A.M., Vital, J., 2006. Transesterification of soybean oil over sulfonic acid functionalised polymeric membranes. Catal Today 118, 166–171. https://doi.org/10.1016/j.cattod.2005.12.012

Han, H., Cao, W., Zhang, J., 2005. Preparation of biodiesel from soybean oil using supercritical methanol and CO2 as co-solvent. Process Biochemistry 40, 3148–3151. https://doi.org/10.1016/j.procbio.2005.03.014

Hanif, M.A., Nisar, S., Rashid, U., 2017. Supported solid and heteropoly acid catalysts for production of biodiesel. Catal Rev Sci Eng 59, 165–188. https://doi.org/10.1080/01614940.2017.1321452

Hino, M., Arata, K., 1988. Synthesis of solid superacid of tungsten oxide supported on zirconia and its catalytic action for reactions of butane and pentane. J Chem Soc Chem Commun 1259–1260. https://doi.org/10.1039/C39880001259

Hu, S., Wang, Y., Han, H., 2011. Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production. Biomass Bioenergy 35, 3627–3635. https://doi.org/10.1016/j.biombioe.2011.05.009

Jeromin, L., Peukert, E., Hilden, Wollmann, G., Duesseldorf, 1987. Process for the pre-esterification of free fatty acids in fats and oils. 4,698,186.

Jiménez-Morales, I., Santamaría-González, J., Maireles-Torres, P., Jiménez-López, A., 2011. Methanolysis of sunflower oil catalyzed by acidic Ta2O 5 supported on SBA-15. Appl Catal A Gen 405, 93–100. https://doi.org/10.1016/j.apcata.2011.07.037

Jiménez-Morales, I., Santamaría-González, J., Maireles-Torres, P., Jiménez-López, A., 2010. Zirconium doped MCM-41 supported WO3 solid acid catalysts for the esterification of oleic acid with methanol. Appl Catal A Gen 379, 61–68. https://doi.org/10.1016/j.apcata.2010.03.001

Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., Jenvanitpanjakul, P., 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chemical Engineering Journal 116, 61–66. https://doi.org/10.1016/j.cej.2005.09.025

Kaur, M., Ali, A., 2011. Lithium ion impregnated calcium oxide as nano catalyst for the biodiesel production from karanja and jatropha oils. Renew Energy 36, 2866–2871. https://doi.org/10.1016/j.renene.2011.04.014

Kaur, M., Malhotra, R., Ali, A., 2018. Tungsten supported Ti/SiO2 nanoflowers as reusable heterogeneous catalyst for biodiesel production. Renew Energy 116, 109–119. https://doi.org/10.1016/j.renene.2017.09.065

Kaur, N., Ali, A., 2015. Preparation and application of Ce/ZrO2-TiO2/SO42- as solid catalyst for the esterification of fatty acids. Renew Energy 81, 421–431. https://doi.org/10.1016/j.renene.2015.03.051

Kesserwan, F., Ahmad, M.N., Khalil, M., El-Rassy, H., 2020. Hybrid CaO/Al2O3 aerogel as heterogeneous catalyst for biodiesel production. Chemical Engineering Journal 385. https://doi.org/10.1016/j.cej.2019.123834

Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K., Lee, J.S., Lee, K.Y., 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst, in: Catalysis Today. pp. 315–320. https://doi.org/10.1016/j.cattod.2004.06.007

Kim, M.Y., Seo, G., Kwon, O.Z., Chang, D.R., 2009. The exceptional activity of a phosphazenium hydroxide catalyst incorporated onto silica in the transesterification of tributyrin with methanol. Chemical Communications 3110–3112. https://doi.org/10.1039/b903969d

Kiss, A.A., Dimian, A.C., Rothenberg, G., 2006. Solid acid catalysts for biodiesel production - Towards sustainable energy. Adv Synth Catal 348, 75–81. https://doi.org/10.1002/adsc.200505160

Kolaczkowski, S.T., Asli, U.A., Davidson, M.G., 2009. A new heterogeneous ZnL2 catalyst on a structured support for biodiesel production. Catal Today 147. https://doi.org/10.1016/j.cattod.2009.07.060

Kouzu, M., Hidaka, J.S., 2012. Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. Fuel 93, 1–12. https://doi.org/10.1016/j.fuel.2011.09.015

Kouzu, M., Nakagaito, A., Hidaka, J.S., 2011. Pre-esterification of FFA in plant oil transesterified into biodiesel with the help of solid acid catalysis of sulfonated cation-exchange resin. Appl Catal A Gen 405, 36–44. https://doi.org/10.1016/j.apcata.2011.07.026

Kurhade, A., Dalai, A.K., 2018. Physiochemical characterization and support interaction of alumina-supported heteropolyacid catalyst for biodiesel production. Asia-Pacific Journal of Chemical Engineering 13. https://doi.org/10.1002/apj.2249

Lanzafame, P., Temi, D.M., Perathoner, S., Centi, G., MacArio, A., Aloise, A., Giordano, G., 2011. Etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol to biodiesel components using mesoporous solid acidic catalysts. Catal Today 175, 435–441. https://doi.org/10.1016/j.cattod.2011.05.008

Latchubugata, C.S., Kondapaneni, R.V., Patluri, K.K., Virendra, U., Vedantam, S., 2018. Kinetics and optimization studies using Response Surface Methodology in biodiesel production using heterogeneous catalyst. Chemical Engineering Research and Design 135, 129–139. https://doi.org/10.1016/j.cherd.2018.05.022

Lee, S.L., Wong, Y.C., Tan, Y.P., Yew, S.Y., 2015. Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. Energy Convers Manag 93, 282–288. https://doi.org/10.1016/j.enconman.2014.12.067

Li, W., Jiang, Z., Ma, F., Su, F., Chen, L., Zhang, S., Guo, Y., 2010. Design of mesoporous SO42−/ZrO2–SiO2(Et) hybrid material as an efficient and reusable heterogeneous acid catalyst for biodiesel production. Green Chemistry 12, 2135–2138. https://doi.org/10.1039/c0gc00144a

Li, Y., Zhang, X.D., Sun, L., Xu, M., Zhou, W.G., Liang, X.H., 2010. Solid superacid catalyzed fatty acid methyl esters production from acid oil. Appl Energy 87, 2369–2373. https://doi.org/10.1016/j.apenergy.2010.01.017

Limmanee, S., Naree, T., Bunyakiat, K., Ngamcharussrivichai, C., 2013. Mixed oxides of Ca, Mg and Zn as heterogeneous base catalysts

for the synthesis of palm kernel oil methyl esters. Chemical Engineering Journal 225, 616–624. https://doi.org/10.1016/j.cej.2013.03.093

Liu, H., Chen, J., Chen, L., Xu, Y., Guo, X., Fang, D., 2016. Carbon Nanotube-Based Solid Sulfonic Acids as Catalysts for Production of Fatty Acid Methyl Ester via Transesterification and Esterification. ACS Sustain Chem Eng 4, 3140–3150. https://doi.org/10.1021/acssuschemeng.6b00156

Liu, R., Wang, X., Zhao, X., Feng, P., 2008. Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel. Carbon N Y 46, 1664–1669. https://doi.org/10.1016/j.carbon.2008.07.016

Liu, X., He, H., Wang, Y., Zhu, S., 2007. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 8, 1107–1111. https://doi.org/10.1016/j.catcom.2006.10.026

Liu, Y., Lotero, E., Goodwin, J.G., Lu, C., 2007. Transesterification of triacetin using solid Brønsted bases. J Catal 246, 428–433. https://doi.org/10.1016/j.jcat.2007.01.006

López, D.E., Goodwin, J.G., Bruce, D.A., 2007a. Transesterification of triacetin with methanol on Nafion® acid resins. J Catal 245, 381–391. https://doi.org/10.1016/j.jcat.2006.10.027

López, D.E., Goodwin, J.G., Bruce, D.A., Furuta, S., 2008. Esterification and transesterification using modified-zirconia catalysts. Appl Catal A Gen 339, 76–83. https://doi.org/10.1016/j.apcata.2008.01.009

López, D.E., Goodwin, J.G., Bruce, D.A., Lotero, E., 2005. Transesterification of triacetin with methanol on solid acid and base catalysts. Appl Catal A Gen 295, 97–105. https://doi.org/10.1016/j.apcata.2005.07.055

López, D.E., Suwannakarn, K., Bruce, D.A., Goodwin, J.G., 2007b. Esterification and transesterification on tungstated zirconia: Effect of calcination temperature. J Catal 247, 43–50. https://doi.org/10.1016/j.jcat.2007.01.003

Lunardi, V.B., Gunawan, F., Soetaredjo, F.E., Santoso, S.P., Chen, C.H., Yuliana, M., Kurniawan, A., Lie, J., Angkawijaya, A.E., Ismadji, S., 2021. Efficient one-step conversion of a low-grade vegetable oil to biodiesel over a zinc carboxylate metal-organic framework. ACS Omega 6, 1834–1845. https://doi.org/10.1021/acsomega.0c03826

Madhuvilakku, R., Piraman, S., 2013. Biodiesel synthesis by TiO2-ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process. Bioresour Technol 150, 55–59. https://doi.org/10.1016/j.biortech.2013.09.087

Majhi, S., Ray, S., 2016. A study on production of biodiesel using a novel solid oxide catalyst derived from waste. Environmental Science and Pollution Research 23, 9251–9259. https://doi.org/10.1007/s11356-015-4824-9

Manríquez-Ramírez, M., Gómez, R., Hernández-Cortez, J.G., Zúñiga-Moreno, A., Reza-San Germán, C.M., Flores-Valle, S.O., 2013. Advances in the transesterification of triglycerides to biodiesel using MgO-NaOH, MgO-KOH and MgO-CeO2 as solid basic catalysts. Catal Today 212, 23–30. https://doi.org/10.1016/j.cattod.2012.11.005

Mansir, N., Taufiq-Yap, Y.H., Rashid, U., Lokman, I.M., 2017. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. Energy Convers Manag 141, 171–182. https://doi.org/10.1016/j.enconman.2016.07.037

Marchetti, J.M., Errazu, A.F., 2008. Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid. Fuel 87, 3477–3480. https://doi.org/10.1016/j.fuel.2008.05.011

Mardhiah, H.H., Ong, H.C., Masjuki, H.H., Lim, S., Lee, H. V., 2017. A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. Renewable and Sustainable Energy Reviews. https://doi.org/10.1016/j.rser.2016.09.036

Marso, T.M.M., Kalpage, C.S., Udugala-Ganehenege, M.Y., 2020. Application of chromium and cobalt terephthalate metal organic frameworks as catalysts for the production of biodiesel from Calophyllum inophyllum oil in high yield under mild conditions. J Inorg Organomet Polym Mater 30, 1243–1265. https://doi.org/10.1007/s10904-019-01251-8

Marwaha, A., Rosha, P., Mohapatra, S.K., Mahla, S.K., Dhir, A., 2018. Waste materials as potential catalysts for biodiesel production: Current state and future scope. Fuel Processing Technology 181, 175–186. https://doi.org/10.1016/j.fuproc.2018.09.011

Mckenzie, A.L., Fishel, C.T., Davis, R.J., 1992. Investigation of the Surface Structure and Basic Properties of Calcined Hydrotalcites. J Catal 138, 547–561.

Meloni, D., Monaci, R., Zedde, Z., Cutrufello, M.G., Fiorilli, S., Ferino, I., 2011. Transesterification of soybean oil on guanidine base-functionalized SBA-15 catalysts. Appl Catal B 102, 505–514. https://doi.org/10.1016/j.apcatb.2010.12.032

Mootabadi, H., Salamatinia, B., Bhatia, S., Abdullah, A.Z., 2010. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 89, 1818–1825. https://doi.org/10.1016/j.fuel.2009.12.023

Nakagaki, S., Bail, A., Santos, V.C. dos, Souza, V.H.R. de, Vrubel, H., Nunes, F.S., Ramos, L.P., 2008. Use of anhydrous sodium molybdate as an efficient heterogeneous catalyst for soybean oil methanolysis. Appl Catal A Gen 351, 267–274. https://doi.org/10.1016/j.apcata.2008.09.026

Nassreddine, S., Karout, A., Lorraine Christ, M., Pierre, A.C., 2008. Transesterification of a vegetal oil with methanol catalyzed by a silica fibre reinforced aerogel encapsulated lipase. Appl Catal A Gen 344, 70–77. https://doi.org/10.1016/j.apcata.2008.04.002

Navajas, A., Campo, I., Moral, A., Echave, J., Sanz, O., Montes, M., Odriozola, J.A., Arzamendi, G., Gandía, L.M., 2018. Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel. Fuel 211, 173–181. https://doi.org/10.1016/j.fuel.2017.09.061

Ngaosuwan, K., Mo, X., Goodwin, J.G., Praserthdam, P., 2010. Effect of solvent on hydrolysis and transesterification reactions on tungstated zirconia. Appl Catal A Gen 380, 81–86. https://doi.org/10.1016/j.apcata.2010.03.030

Ni, J., Meunier, F.C., 2007. Esterification of free fatty acids in sunflower oil over solid acid catalysts using batch and fixed bed-reactors. Appl Catal A Gen 333, 122–130. https://doi.org/10.1016/j.apcata.2007.09.019

Nikseresht, A., Daniyali, A., Ali-Mohammadi, M., Afzalinia, A., Mirzaie, A., 2017. Ultrasound-assisted biodiesel production by a novel composite of Fe(III)-based MOF and phosphotangestic acid as efficient and reusable catalyst. Ultrason Sonochem 37, 203–207. https://doi.org/10.1016/j.ultsonch.2017.01.011

Nowicki, J., Lach, J., Organek, M., Sabura, E., 2016. Transesterification of rapeseed oil to biodiesel over Zr-dopped MgAl hydrotalcites. Appl Catal A Gen 524, 17–24. https://doi.org/10.1016/j.apcata.2016.05.015

OECD/FAO, 2021. OECD-FAO Agricultural Outlook 2021-2030, OECD-FAO Agricultural Outlook. OECD, Paris. https://doi.org/10.1787/19428846-en

Omar, W.N.N.W., Amin, N.A.S., 2011. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. Fuel Processing Technology 92, 2397–2405. https://doi.org/10.1016/j.fuproc.2011.08.009

Omota, F., Dimian, A.C., Bliek, A., 2003. Fatty acid esterification by reactive distillation: Part 2 - kinetics-based design for sulphated zirconia catalysts. Chem Eng Sci 58, 3175–3185. https://doi.org/10.1016/S0009-2509(03)00154-4

Pandit, P.R., Fulekar, M.H., 2017. Egg shell waste as heterogeneous nanocatalyst for biodiesel production: Optimized by response surface methodology. J Environ Manage 198, 319–329. https://doi.org/10.1016/j.jenvman.2017.04.100

Pangestu, T., Kurniawan, Y., Soetaredjo, F.E., Santoso, S.P., Irawaty, W., Yuliana, M., Hartono, S.B., Ismadji, S., 2019. The synthesis of biodiesel using copper based metal-organic framework as a catalyst. J Environ Chem Eng 7. https://doi.org/10.1016/j.jece.2019.103277

Pârvulescu, V.I., Pârvulescu, V., Endruschat, U., Granger, P., Richards, R., 2007. Mesoporous Pt-SiO2 and Pt-SiO2-Ta2O 5 catalysts prepared using Pt colloids as templates. ChemPhysChem 8, 666–678. https://doi.org/10.1002/cphc.200600571

Pasias, S., Barakos, N., Alexopoulos, C., Papayannakos, N., 2006. Heterogeneously catalyzed esterification of FFAs in vegetable oils. Chem Eng Technol 29, 1365–1371. https://doi.org/10.1002/ceat.200600109

Pimentel, D., Patzek, T.W., 2005. Ethanol production using corn, switchgrass, and wood; Biodiesel production using soybean and sunflower. Natural Resources Research 14, 65–76. https://doi.org/10.1007/s11053-005-4679-8

Rahadi, A.N., Martinus, J.J., Santoso, S.P., Yuliana, M., Kurniawan, A., Gunarto, C., Hartono, S.B., Soetaredjo, F.E., Ismadji, S., 2021. Double-shelled hollow mesoporous silica incorporated copper (II) (Cu/DS-HMS-NH2) as a catalyst to promote in-situ esterification/transesterification of low-quality palm oil. Int J Energy Res 45, 19929–19946. https://doi.org/10.1002/er.7064

Ropero-Vega, J.L., Aldana-Pérez, A., Gómez, R., Niño-Gómez, M.E., 2010. Sulfated titania [TiO2/SO42-]: A very active solid acid catalyst for the esterification of free fatty acids with ethanol. Appl Catal A Gen 379, 24–29. https://doi.org/10.1016/j.apcata.2010.02.020

Roschat, W., Phewphong, S., Khunchalee, J., Moonsin, P., 2018. Biodiesel production by ethanolysis of palm oil using SrO as a basic heterogeneous catalyst. Mater Today Proc 5, 13916–13921.

Roschat, W., Siritanon, T., Yoosuk, B., Promarak, V., 2016. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. Energy Convers Manag 108, 459–467. https://doi.org/10.1016/j.enconman.2015.11.036

Rosset, I.G., Tavares, M.C.H., Assaf, E.M., Porto, A.L.M., 2011. Catalytic ethanolysis of soybean oil with immobilized lipase from Candida antarctica and 1H NMR and GC quantification of the ethyl esters (biodiesel) produced. Appl Catal A Gen 392, 136–142. https://doi.org/10.1016/j.apcata.2010.10.035

Russbueldt, B.M.E., Hoelderich, W.F., 2009. New sulfonic acid ion-exchange resins for the preesterification of different oils and fats with high content of free fatty acids. Appl Catal A Gen 362, 47–57. https://doi.org/10.1016/j.apcata.2009.04.019

Salinas, D., Sepúlveda, C., Escalona, N., GFierro, J.L., Pecchi, G., 2018. Sol–gel La2O3–ZrO2 mixed oxide catalysts for biodiesel production. Journal of Energy Chemistry 27, 565–572. https://doi.org/10.1016/j.jechem.2017.11.003

Santiago-Torres, N., Romero-Ibarra, I.C., Pfeiffer, H., 2014. Sodium zirconate (Na2ZrO3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. Fuel Processing Technology 120, 34–39. https://doi.org/10.1016/j.fuproc.2013.11.018

Santosa, F.H., Laysandra, L., Soetaredjo, F.E., Santoso, S.P., Ismadji, S., Yuliana, M., 2019. A facile noncatalytic methyl ester production from waste chicken tallow using single step subcritical methanol: Optimization study. Int J Energy Res 43, 8852–8863. https://doi.org/10.1002/er.4844

Semwal, S., Arora, A.K., Badoni, R.P., Tuli, D.K., 2011. Biodiesel production using heterogeneous catalysts. Bioresour Technol 102, 2151–2161. https://doi.org/10.1016/j.biortech.2010.10.080

Shi, G., Yu, F., Wang, Y., Pan, D., Wang, H., Li, R., 2016. A novel one-pot synthesis of tetragonal sulfated zirconia catalyst with high activity for biodiesel production from the transesterification of soybean oil. Renew Energy 92, 22–29. https://doi.org/10.1016/j.renene.2016.01.094

Siddiquee, M.N., Kazemian, H., Rohani, S., 2011. Biodiesel production from the lipid of wastewater sludge using an acidic heterogeneous catalyst. Chem Eng Technol 34, 1983–1988. https://doi.org/10.1002/ceat.201100119

Sirisomboonchai, S., Abuduwayiti, M., Guan, G., Samart, C., Abliz, S., Hao, X., Kusakabe, K., Abudula, A., 2015. Biodiesel production from waste cooking oil using calcined scallop shell as catalyst. Energy Convers Manag 95, 242–247. https://doi.org/10.1016/j.enconman.2015.02.044

Soumanou, M.M., Bornscheuer, U.T., 2003. Improvement in lipase-catalyzed synthesis of fatty acid methyl esters from sunflower oil. Enzyme Microb Technol 33, 97–103. https://doi.org/10.1016/S0141-0229(03)00090-5

Sreeprasanth, P.S., Srivastava, R., Srinivas, D., Ratnasamy, P., 2006. Hydrophobic, solid acid catalysts for production of biofuels and lubricants. Appl Catal A Gen 314, 148–159. https://doi.org/10.1016/j.apcata.2006.08.012

Suryajaya, S.K., Mulyono, Y.R., Santoso, S.P., Yuliana, M., Kurniawan, A., Ayucitra, A., Sun, Y., Hartono, S.B., Soetaredjo, F.E., Ismadji, S., 2021. Iron (II) impregnated double-shelled hollow mesoporous silica as acid-base bifunctional catalyst for the conversion of low-quality oil to methyl esters. Renew Energy 169, 1166–1174. https://doi.org/10.1016/j.renene.2021.01.107

Suryaputra, W., Winata, I., Indraswati, N., Ismadji, S., 2013. Waste capiz (Amusium cristatum) shell as a new heterogeneous catalyst for biodiesel production. Renew Energy 50, 795–799. https://doi.org/10.1016/j.renene.2012.08.060

Teo, S.H., Rashid, U., Thomas Choong, S.Y., Taufiq-Yap, Y.H., 2017. Heterogeneous calcium-based bimetallic oxide catalyzed transesterification of Elaeis guineensis derived triglycerides for biodiesel production. Energy Convers Manag 141, 20–27. https://doi.org/10.1016/j.enconman.2016.03.042

Tesser, R., Di Serio, M., Guida, M., Nastasi, M., Santacesaria, E., 2005. Kinetics of oleic acid esterification with methanol in the presence of triglycerides. Ind Eng Chem Res 44, 7978–7982. https://doi.org/10.1021/ie050588o

Tichit, D., Lhouty, M.H., Guida, A., Chiche, B.H., Figueras, F., Auroux, A., Bartalini, D., Garrone, E., 1995. Textural properties and catalytic activity of hydrotalcites. J Catal 151, 50–59.

Timorria, I.F., 2021. Kemendag: Harga pangan dunia diperkirakan mulai stabil 2022 [WWW Document]. Bisnis.com. URL https://ekonomi.bisnis.com/read/20210604/12/1401480/kemendag-harga-pangan-dunia-diperkirakan-mulai-stabil-2022 (accessed 3.10.23).

Trakarnpruk, W., Porntangjitlikit, S., 2008. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renew Energy 33, 1558–1563. https://doi.org/10.1016/j.renene.2007.08.003

Vaccari, A., 1999. Clays and catalysis: A promising future. Appl Clay Sci 14, 161–198.

Valvekens, P., Vermoortele, F., De Vos, D., 2013. Metal-organic frameworks as catalysts: The role of metal active sites. Catal Sci Technol 3, 1435–1445. https://doi.org/10.1039/c3cy20813c

Watanabe, Y., Shimada, Y., Sugihara, A., Noda, H., Fukuda, H., Tominaga, Y., 2000. Continuous production of biodiesel fuel from vegetable oil using immobilized Candida antarctica lipase. J Am Oil Chem Soc 77, 355–360.

Watanabe, Y., Shimada, Y., Sugihara, A., Tominaga, Y., 2001. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor. J Am Oil Chem Soc 78, 703–707.

Xie, W., Wan, F., 2019. Immobilization of polyoxometalate-based sulfonated ionic liquids on UiO-66-2COOH metal-organic frameworks for biodiesel production via one-pot transesterification-esterification of acidic vegetable oils. Chemical Engineering Journal 365, 40–50. https://doi.org/10.1016/j.cej.2019.02.016

Yadav, G.D., Thathagar, M.B., 2002. Esterification of maleic acid with ethanol over cation-exchange resin catalysts. React Funct Polym 52, 99–110.

Yaşar, F., 2019. Biodiesel production via waste eggshell as a low-cost heterogeneous catalyst: Its effects on some critical fuel properties and comparison with CaO. Fuel 255. https://doi.org/10.1016/j.fuel.2019.115828

Yoo, S.J., Lee, H. shik, Veriansyah, B., Kim, J., Kim, J.D., Lee, Y.W., 2010. Synthesis of biodiesel from

rapeseed oil using supercritical methanol with metal oxide catalysts. Bioresour Technol 101, 8686–8689. https://doi.org/10.1016/j.biortech.2010.06.073

Yuliana, M., Santoso, S.P., Soetaredjo, F.E., Ismadji, S., Ayucitra, A., Angkawijaya, A.E., Ju, Y.H., Tran-Nguyen, P.L., 2020. A one-pot synthesis of biodiesel from leather tanning waste using supercritical ethanol: Process optimization. Biomass Bioenergy 142. https://doi.org/10.1016/j.biombioe.2020.105761

Zafiropoulos, N.A., Ngo, H.L., Foglia, T.A., Samulski, E.T., Lin, W., 2007. Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks. Chemical Communications 3670–3672. https://doi.org/10.1039/b704189f

Zeng, H. yan, Liao, K. bo, Deng, X., Jiang, H., Zhang, F., 2009. Characterization of the lipase immobilized on Mg-Al hydrotalcite for biodiesel. Process Biochemistry 44, 791–798. https://doi.org/10.1016/j.procbio.2009.04.005

Zhang, G., Hattori, H., Tanabe, K., 1988. Aldol Addition of Acetone, Catalyzed by Solid Base Catalysts: Magnesium Oxide, Calcium Oxide, Strontium Oxide, Barium Oxide, Lanthanum (III) Oxide and Zirconium Oxide. Appl Catal 36, 189.

Zhang, Q., Lei, D., Luo, Q., Wang, J., Deng, T., Zhang, Y., Ma, P., 2020. Efficient biodiesel production from oleic acid using metal-organic framework encapsulated Zr-doped polyoxometalate nano-hybrids. RSC Adv 10, 8766–8772. https://doi.org/10.1039/d0ra00141d

Zięba, A., Drelinkiewicz, A., Konyushenko, E.N., Stejskal, J., 2010. Activity and stability of polyaniline-sulfate-based solid acid catalysts for the transesterification of triglycerides and esterification of fatty acids with methanol. Appl Catal A Gen 383, 169–181. https://doi.org/10.1016/j.apcata.2010.05.042