Solid Catalyst in Esterification and Transesterification Reactions for Biodiesel Production: A Review

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Abstract - Biodiesel is considered as an important substitute for the replacement of fossil diesel due to its biodegradable, renewable and non-toxicity to environment. Biodiesel consist of mixture of mono alkyl esters of long chain fatty acids. It is produced from vegetable oils, animal fats and waste cooking oil. Solid catalysts are promising and advantageous for biodiesel production because those could be reusable, environmentally benign and are more effective than liquid catalysts. Moreover, the application of solid catalysts does not produce soaps through triglycerides saponification or free fatty acids neutralization. When triglycerides as major component of oil react with alcohol (methanol or ethanol) to form biodiesel in the presence of base catalyst, this called is transesterification. When acid catalysts are used for reducing free fatty acids to form biodiesel, this called is esterification. The application of solid catalysts in esterification and transesterification reactions for biodiesel production are discussed in this review.

Index of Terms **-** biodiesel, esterification, solid catalyst, transesterification

I. INTRODUCTION

Biodiesel is fuels from biological feedstocks such as virgin vegetable oils (edible and non-edible), animal fats and waste cooking oil because of its chemical components is the same as fossil diesel (diesel engine) [1-3]. Biodiesel consist of mixture of mono alkyl esters of long chain fatty acids [3, 4]. Synthesizing biodiesel process such as direct use and blending, micro-emulsions, thermal cracking (pyrolysis) and transesterification. The most popular of them is transesterification due to its simple method application, normally condition processing, highest conversion efficiency and best quality of biodiesel [5]. In transesterification method, biodiesel produced by triglycerides as major component oil react with short chain of alcohol (methanol or ethanol) in the presence of catalyst [2, 3, 6, 7]. Catalyst increased the rate of reaction to produce methyl esters (biodiesel) [3].

Biodiesel (*fatty acid alkyl ester*, FAAE) and by-products of glycerol are produced by transesterification process, when triglycerides react with methanol or ethanol in the presence of base catalyst [3]. When free fatty acids (FFAs) in oil more than 1%, acid catalysts are used for reducing FFAs to form FAAE and water, this called is esterification [8]. Many advantageous of biodiesel such as biodegradable, renewable, non-toxicity, free of aromatics and sulphur, environmentally benign, more combustion efficiency, more cetane number, more flash point and 10-11% oxygen content per mass [2, 9]. Physico-chemical properties of biodiesel are similar chemical compositions of conventional diesel fuels, so that biodiesel can be used as pure biodiesel (B100) or mixed fossil diesel in non-modification of compression engine [10, 11].

Conventional catalysts (homogeneous catalysts) in transesterification for biodiesel production are liquid base catalysts (such as NaOH or KOH) and liquid acid catalysts (such as H_2SO_4 or HCl) [12, 13]. These are more reactive in reactions so that can produce high mass yield of biodiesel (more than 85%). However, according to Xie and Li (2006), biodiesel conversion from soybean oil in liquid base catalyst has some weakness such as difficult to regenerate and also provide rise to serious environment [6], operating at high temperature and corrosive problems in engine [14, 15]. Solid catalysts are chosen for substituting liquid catalysts. Therefore, solid catalysts could be reused, environmentally benign and are more effective in separation from product reaction and non-corrosive problems [16, 17]. Moreover, the application of solid catalysts does not produce soaps through triglycerides saponification or FFAs neutralization [18].

This review focus on discussed the application of solid catalysts in esterification and transesterification reactions for biodiesel production from feedstocks of virgin vegetable oils, animal fats

and waste cooking oil. The types of solid catalyst for biodiesel production in reaction conditions such as catalyst amount to oil, methanol to oil molar ratio, reaction time, reaction temperature and mixing intensity would be also highlighted.

II. METHODS

This review was performed by exploring the compilation of literatures related to the study field from reading sources such as articles, journals, and other online sources. Initial topic will cover: (1) application of solid catalysts in esterification and transesterification reactions for biodiesel production from feedstocks of virgin vegetable oils, animal fats and waste cooking oil and (2) reaction conditions such as catalyst amount to oil, methanol to oil molar ratio, reaction time, reaction temperature and mixing intensity.

III. DISCUSSION

Nowadays, the use of solid catalysts for biodiesel production are extensively studied by many researchers. Types of solid catalyst in esterification and transesterification reactions for biodiesel production from vegetable oils, animal fats and waste cooking oil are solid catalysts of inorganic acid (acid catalyst, sulfonic acid groups and carbon-based solid acid) and basic solid catalysts (metal oxide, alkaline-earth metal species, supported metal oxide, transition metal oxides and mixed metal oxides) [1, 2, 8]. The application of solid catalysts for alcoholysis (methanolysis or ethanolysis) are complexities process relatively, because of its process takes place in a three-phase system such as solid catalyst and two phase liquid mixture (oil and alcohol). Also, alcoholysis takes place in a partial reaction between triglycerides saponification and methyl esters as well as neutralization of free fatty acids by catalyst. Efficiency of solid catalyst can be determined by many factors such as specific surface area, porosity (pore diameter, pore volume and pore size distribution) and active sites amount. Structure of active sites in solid catalyst prepared by positive metal ions (cations) that consists of Lewis acid sites as electron acceptors and negative oxygen ions (anions) that consists of Bronsted base sites and Lewis base sites as proton acceptors [2]. The use of them have been reported in this literature review.

3.1 Solid Catalysts in Esterification Reaction for Biodiesel Production

The application of solid catalysts in esterification process for biodiesel production has been reported in the literatures as follows. Hidayat *et al*. (2015) synthesized solid catalyst of sulfonating the coconut shell biochar for esterification of palm fatty acid distillate high FFAs to form biodiesel. Sulfonating process of the coconut shell biochar prepared by concentrate sulfuric acid. The result of this research showed that yield of biodiesel was 87% within optimum reaction conditions were the amounts of catalyst to oil 7%, methanol to oil molar ratio 12:1, reaction time at 4 hours and reaction temperature at 60^{o}C [19].

Rachmat *et al*. (2017) studied esterification lauric acid to biodiesel by solid catalyst of sulfated zirconia mesopore prepared from cetyl trimethyl ammonium bromide (CTAB) and $(NH_4)_2SO_4$. Solid catalyst synthesized by template-assisted on variation of temperature calcination (400-700^{o}C) and ratio variation of zirconia and CTAB. Its result obtained that sulfated zirconia mesopores (MZS) at ratio 3:1 was optimum specific surface area, pore diameter and pore volume of 147.5 m^2/g, 6.6 nm and 0.396 cc/g respectively. The yield of methyl lauric of 89.8% was achieved by MZS-600 solid catalyst prepared using CTAB to zirconyl of ratio 9:1 [20].

Jha and Sontakke (2018) demonstrated the solid catalyst of sulfuric acid activated coconut coir char in esterification process of waste cooking oil to form biodiesel. The synthesis of catalyst prepared by sulfonated coconut coir char and pyrolysis at 500^{o}C in 3 hours. The result showed that yield mass of biodiesel 90.12 wt. % within optimum reaction conditions were the catalyst loading 5%, methanol to oil molar ratio 18:1, reaction time at 7 hours and reaction temperature at 65^{o}C [21].

Gardy *et al*. (2018) investigated SO_4/Fe-Al-TiO_2 as a solid catalyst for esterification of waste cooking oil to biodiesel. The yield FAME of 95.6% within reaction time at 2.5 hours, reaction temperature 90^{o}C, the catalyst amounts to oil 3% and methanol to oil molar ratio of 10:1. The solid catalyst of SO_4/Fe-Al-TiO_2 presented excellent stability and maintaining a high performance in the presence of up to 20 wt.% oleic acid and relatively stable for over 10 reactions cycles with waste cooking oil [22].

Hossain *et al*. (2019) studied synthesis, characterization and application of solid acid catalyst S-TiO_2/SBA-15 (*Santa Barbara amorphous*-15) in an esterification hydrolyzed waste cooking oil to biodiesel. The yield of biodiesel was 94.96 ± 0.12% obtained under the optimum reaction conditions at 200◦C, time reaction at 30 minutes and methanol molar ratio to oil of 15:1 with solid catalyst loading of 1.0%. Its catalyst was reused in three times with efficiency of 90% without regeneration process [23].

Balotin *et al*. (2020) studied esterification reaction of oleic acid and methanol using solid catalyst based on different sulfonated carbon nanostructures (graphene, nanotube, nano-onions and nanographite) to produce biodiesel. The result was obtained that biodiesel conversion of 95 % with methanol to oil molar ratio of 10:1 by using catalyst amount to oil of 2.5 wt.% at 100°C for 3 hours. The reuse reactions described that the activity of catalytic process decreased to 20% after 4 cycles used [24].

3.2 Solid Catalysts in Transesterification Reaction for Biodiesel Production

The application of solid catalysts in transesterification process for biodiesel production has been reported in the literatures as follows. Lam and Lee (2011) studied solid catalyst of $SO_4^{2-}/SnO_2/SiO_2$ for converting waste cooking oil to biodiesel in transesterification reaction. The result showed that biodiesel yield was 81.4%, 6% of catalyst to oil (wt.%), methanol:ethanol to oil molar ratio of 9:6:1, reaction temperature at 150ºC and reaction time of 1 hour [25].

Chen *et al*. (2013) investigated transesterification soybean cooking oil into biodiesel using Li-modified *rice hush ash* (RHA) and methanol at atmospheric pressure. Synthesis of solid catalyst was done by a simple method of solid state reaction, with mixture 1.00 g RHA and 1.23 g Li_2CO_3 calcinated at 900ºC in air for 4 hours. Its result showed that catalyst was highly active of basic strength (H_) exceeded 15.0. The catalyst was also air-insensitive, as only a few CO_3^{2-} anions formed on catalyst surface after exposure to air for 72 hours and no obvious LiOH formed on its surface. The optimal reaction conditions of methanol to oil molar ratio was 24:1, 4% catalyst amount and a reaction temperature of 65ºC for 3 hours with 99.5% biodiesel conversion [26].

Silva *et al*. (2014) examined three types of smectites clays in different compositions treated with potassium fluoride (KF) as solid catalysts. Those catalysts were used in transesterification reaction of soybean oil with methanol to methyl esters (biodiesel). Design of experimental was applied to evaluate the effect of the variables of transesterification reaction such as mass catalyst ratio to oil, methanol to oil molar ratio and reaction temperature. Results indicated that increasing ratio of SiO_2/Al_2O_3 ratio in smectites caused an increase in catalyst basicity and conversion rate into methyl esters. The conversion maximum of oil to biodiesel was 89.19%, catalyst amount to oil of 25%, alcohol to oil molar ratio of 9:1 and temperature reaction at 353K [17].

Kaur and Ali (2015) investigated solid catalyst of Li/NiO nano-particle for ethanolysis of vegetable oils to biodiesel production. The solid catalyst was synthesized by ceramics method with wet impregnation of Li on NO and using transesterification reaction of waste cottonseed oil into biodiesel. The result exhibited that optimized reaction conditions were 5% (wt.%) catalyst, ethanol to oil molar ratio of 12:1 and reaction temperature at 65°C with >98% biodiesel yield at 3 hours as well as through pseudo first reaction and activation energy of 74.2 kJ/mole [27].

Amos *et al*. (2016) studied preparation of bio-catalyst base on *cocoa pod ash* (CPA) and *rice hush ash* (RHA) for using transesterification reaction of *Parinari polyandra* seed oil to biodiesel compared with conventional catalyst of KOH solution. Synthesis of solid catalyst from CPA and RHA were become ash in muffle furnace at 600ºC and source of oil collected with extraction of *Parinari polyandra* to produce biodiesel in transesterification reaction. The analysis result indicated that metal composition of CPA as potassium of 13.05 ppm, sodium of 6.65 ppm meanwhile RHA contained potassium of 3.24 ppm, sodium of 1.748 ppm, iron of 0.053 ppm, magnesium of 1.575 ppm, calcium of 2.325 ppm and aluminum of 0.009 ppm. Various concentrations of KOH, CPA and RHA were investigated 0.5-0.4%. Optimization conditions of biodiesel production were methanol to oil molar ratio of 6:1 with 1% KOH, 2% RHA and 4% CPA catalysts provided good yields. The biodiesel yields of 99.94, 98.61 and 88.85% were obtained with 1% KOH, 4% CPA and 2% RHA catalysts respectively [28].

Mabitla *et al*. (2016) examined solid catalyst activity of pure sodium silicate for transesterification reaction of animal fat (beef tallow) to biodiesel. In transesterification reactions optimization of its animal fat were obtained biodiesel yield of 15.5% (17.1% for 1 g of catalyst), reaction temperature of 62ºC and methanol to oil molar ratio of 8:1. The biodiesel yield increased with increasing catalyst amount and reaction time. The maximum recovery of catalyst was achieved 82% for 1 g catalyst. Therefore, its solid catalyst is recyclable and reused [29]. The same research was conducted by Wendi *et al*. (2014) to investigate solid catalyst of CaO from eggshell in transesterification reaction of waste animal fat (beef) with started by esterification reaction of free fatty acids liquid catalyst of 0.5% sulfuric acid. The result showed that biodiesel yield of 82.43%, methanol to oil molar ratio of 9:1, catalyst amount to oil of 3%, reaction time of 1.5 hours and reaction temperature of 55ºC [30].

Lestari *et al*. (2017) synthesized solid catalyst of lithium modified-rise hush ash for transesterification reaction of *Pongamia* seed oil into biodiesel. Biodiesel yield in transesterification was 83.6% with methanol to oil molar ratio of 5:1, reaction temperature of 60ºC, mixing intensity of 600 rpm in reaction process of 180 minutes. This solid catalyst provides constant performance with more than 3 times of reuse to produce biodiesel [31].

Widayat *et al*. (2017) studied solid catalyst of fly ash and limestone mixture for biodiesel production from vegetable oil in transesterification reaction with started by esterification reaction of sulfuric acid liquid catalyst. Biodiesel yield in transesterification reaction was 83.6% with methanol to oil molar ratio of 5:1, reaction temperature of 60ºC and mixing intensity of 600 rpm in reaction process at 180 minutes. This solid catalyst provides constant performance with more than 3 times of reuse to produce biodiesel [32].

Solis *et al*. (2017) synthesized solid catalyst of Li_2O/Al_2O_3 and MgO/Al_2O_3 in transesterification

reaction of rapeseed oil to biodiesel. The test catalyst result was obtained that biodiesel yield of 98% with Li_2O/Al_2O_3 catalyst at methanol to oil molar ratio of 6:1, catalyst amount to oil of 5%, reaction time of 2 hours, reaction temperature of 60ºC and mixing intensity of 180 rpm [33].

Varghese *et al*. (2017) conducted comparation of CuO solid nano-catalyst with NaOH liquid catalyst (conventional catalyst) for transesterification reaction of coconut oil into biodiesel. Synthesis of solid catalyst prepared by simple precipitation method. The result showed that the CuO nano-particle formation of needle-like in shape. The catalyst optimum of biodiesel production was CuO catalyst to oil ratio of 4:1 and NaOH catalyst to oil ratio of 17:1. The GC-MS analysis of FAME components was obtained that 86.56% for CuO and 79.52% for NaOH catalysed respectively. From the FTIR analysis was presence of two functional groups, such as methyl (CH_3) and ester (C-O ester) [34].

Borah *et al*. (2017) explored nano-solid catalyst of TiO_2-ZnO for biodiesel production from non-edible oil of *Thevetia Peruviana* in transesterification reaction. The solid catalyst of TiO_2-ZnO prepared by sol-gel method. The result was obtained that biodiesel conversion of 94.11% with reaction conditions namely 5% catalyst to oil ratio, methanol to oil molar ratio of 6:1, reaction temperature of 60ºC, reaction time of 5 hours in 600 rpm agitated [35].

Simpen *et al*. (2018) studied solid nano-catalyst of biohydroxyapatite-lithium which was prepared from extracted bovine bone waste and modified lithium for converting malapari seed oil (*Milletia* pinnata L.) to biodiesel. The result presented that mass yield of biodiesel was 88.86% with reaction conditions such as catalyst amount to oil of 5%, methanol to oil molar ratio of 8:1, reaction temperature of 65ºC and reaction time at 150 hours. The GC-MS analysis of biodiesel showed 5 in main peaks exhibiting as methyl oleic, methyl erusic, methyl palmitic, methyl linoleic and stearic [36].

Hartono *et al*. (2018) synthesized solid catalyst of natural zeolite/KOH using ion exchanger for biodiesel production from vegetable oil in transesterification reaction. The biodiesel production was reached optimum reaction conditions, namely biodiesel yield of 98.88% and methanol to oil molar ratio of 7:1 [37].

Utubira *et al*. (2018) investigated biodiesel production from palm oil in transesterification reaction using solid catalyst of KOH/ZrO_2-bentonite. Solid catalyst was prepared with impregnation method of KOH on ZrO_2-bentonite at ratio KOH to ZrO_2-bentonite was 20-30 wt.% with the heating process using 700 W microwave radiation for 10 minutes. Activity catalytic obtained that biodiesel yield was 81% with reaction conditions were catalyst amount to oil of 3%, reaction temperature of 65ºC, reaction time of 3 hours. The ASTM test of biodiesel well agreement with Indonesian National Standard (SNI 04-7182-2006) of diesel oil [38].

Astuti *et al*. (2019) studied solid catalyst of CaO from crab shell K_2O-modified for converting rubber seen oil (*Hevea brasiliensis*) to biodiesel in transesterification reaction. In the initial process was begun esterification reaction of oil by sulfuric acid of 1% concentration. The solid catalyst examination results showed that the optimum of catalyst amount to oil of 3%, methanol to oil molar ratio of 1:9, reaction temperature at 60ºC and reaction time of 2 hours with biodiesel yield was 91.05%. The biodiesel compositions were stearic methyl ester, linoleic methyl ester, linolenic methyl ester and palmitic methyl ester [39].

Pratigto and Istadi (2019) investigated solid base catalyst of CaO calcinated from pure $CaCO_3$ for kinetics of transesterification reaction of soybean oil into biodiesel production. The kinetics reaction was studied mole reactant ratio at reaction temperature of 60°C, catalyst amount to oil of 3 wt.% and reaction time of 180 minutes. The dependency of reaction rate to the reactants described that methanol was adsorbed on the catalyst surface and triglycerides were not adsorbed on its surface. The possible reaction mechanism follows the Eley-Rideal mechanism model [40].

Taslim *et al*. (2019) assessed solid catalyst activity of natural zeolite of KOH modified for transesterification reaction of rice bran oil to biodiesel. The result showed that methyl esters yield was 98.78% with optimum reaction conditions such as mass catalyst to oil ratio of 2%, methanol to oil molar ratio of 10:1, reaction time of 120 minutes at 60ºC and 500 rpm agitated. The assessment result on biodiesel properties such as density, viscosity, purity and flash point good agreement to the Indonesian National Standard (SNI) [41].

Ortega *et al*. (2019) applied solid catalyst of Co/Fe-mixed oxides different ratio on the precursors for transesterification reaction of waste cooking oil into biodiesel. The solid catalyst was synthesized into co-precipitates method. The result showed that biodiesel conversion of 96% with reaction conditions were reaction time of 20 minutes, catalyst amount to oil ratio of 2%, methanol to oil molar ratio of 6:1 at 65ºC. The catalyst contains a mixture of amorphous phases and predominant crystalline of $CoFe_2O_4$ and Na_xCoO_2 [42].

Herlina *et al*. (2019) studied solid catalyst of sulfated silica (SiO_2/SO_3H^+) for coconut oil transesterification reaction to biodiesel. The silica extracted from *Sugarcane Bagasse* and calcinated at 700ºC. The analysis result of FTIR indicated the presence of 1126.43 cm^{-1} absorption band, which is associated with S=O group, in sulfated silica spectra, meanwhile in the pure silica, this band is not detected. The GC-MS analysis described that transesterification reaction with its solid catalyst to

biodiesel production successfully. Optimum reaction conditions were obtained namely mass catalyst to oil ratio of 1%, methanol to oil molar ratio of 6:1, reaction temperature at 60-65^{o}C, reaction time of 2 hours and mixing intensity of 600 rpm with biodiesel conversion of 89% [43].

Al-Ani *et al*. (2019) synthesized nano-crystalline of CsK-zeolite from Na-zeolite and K modified as solid catalyst for biofuel production in transesterification reaction. The catalyst was produced by converting Na-zeolite into the K forms and then exchanging with the Cs-containing solution and calcinated at 450^{o}C for 2 hours. Converting bio-oil to biofuel in reaction conditions such as methanol to oil molar ratios of 6:1, 9:1 and 12:1, at temperatures range of 100-160^{o}C for 1 hour and mass catalyst to oil ratios of 1-5%. The application of solid catalyst for biofuel production successfully in conversion of 98% and selectivity of 99% [44].

Mohamed *et al*. (2019) examined solid catalyst activity of sulfonated rice straw (RS-SO_3H) for transesterification reaction of waste cooking oil into biodiesel. The factors affecting in process of transesterification reaction namely reaction time, reaction temperature, catalyst amount to oil and methanol to oil molar ratio were studied. The result of RS-SO_3H activity was mass yield of biodiesel extended to 90.37% and FAME content of 91.38%, mass catalyst to oil ratio of 10%, methanol to oil molar ratio of 20:1, reaction time of 6 hours at 70^{o}C and 7 cycles life-time maximum [11].

Ulfah *et al*. (2019) studied ability of sulfated gamma alumina (γ-Al_2O_3) solid catalyst for transesterification reaction of waste cooking oil into biodiesel. The results of optimum conditions for esterification reaction using sulfated alumina catalyst showed that catalyst amount to oil was 1 wt.%/v, methanol to oil volume ratio was 1.5, reaction time of 1 hour, reaction temperature of 60^{o}C and 400 rpm agitated with biodiesel yield was 66.67%. In the initial process, waste cooking oil was prepared by mixture of 85% phosphate acid (mixture ratio to oil of 0.5%) [45].

Degfie *et al*. (2019) investigated solid catalyst of CaO synthesis for biodiesel production from waste cooking oil in esterification reaction. The testing solid catalyst result was obtained that biodiesel yield of 96%, reaction temperature of 50°C, methanol to oil molar ratio of 8:1, catalyst amount to oil of 1%, reaction time of 90 minutes and mixing intensity of 1500 rpm. The reaction conditions were carried out in under atmospheric pressure. The properties of biodiesel were tested according to the Fuel Standards of American (ASTM D6571) [46].

As the research result of those researchers showed that the affecting factors in biodiesel production determine performance of solid catalyst in esterification and transesterification reactions. High performance of solid catalyst is reached when producing high biodiesel yield in minimum methanol to oil molar ratio, low catalyst amount in loading, minimum reaction time, low reaction temperature and low mixing intensity. Reviewed results from studied researchers were obtained range biodiesel yield of 66-99.5%, methanol to oil molar ratio range of 4:1-24:1, ethanol to oil molar ratio of 12:1, ethanol/methanol to oil molar ratio of 9:6:1, catalysts amount to oil range of 1-10% (wt.%), reaction times range of 30-180 minutes, reaction temperature range of 50-200^{o}C and mixing intensity range of 180-1500 rpm. Therefore, solid catalysts are suitable to explore for converting vegetable oils, animal fats and waste cooking oil to biodiesel in esterification and transesterification reactions.

IV. CONCLUSION

Biodiesel is alternative fuels for the replacement of fossil diesel due to its biodegradable, renewable and non-toxicity to environment, so that become focus interest in this study. Biodiesel and glycerol are produced by transesterification process, when triglycerides react with methanol or ethanol in the presence of base catalyst. When FFAs in oil more than 1%, acid catalysts in esterification reaction are used for its reducing to form biodiesel and water. Solid catalysts have more potencial and advatageous than liquid catalysts, because they could be reused, environmentally benign and are more effective in separation from product reaction and non-corrosive problems. Therefore, the improvement of solid catalysts to produce biodiesel economically have been continuous depeloped by researchers.

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