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Submission ID: 1403178031

File name: 019_Asri_2020_IOP_Conf._Ser.__Earth_Environ._Sci._460_012033.pdf (933.58K)

Word count: 5947

Character count: 31333

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To cite this article: N P Asri *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **460** 012033

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Transesterification of kesambi oil (*Schleichera oleosa l.*) using nano ZnO-CuO/ γ -alumina solid catalyst

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Abstract. Nano alumina-supported zinc oxide-copper oxide (ZnO-CuO/ γ -Al₂O₃) solid catalyst that is coded by NZCA, has been successfully synthesized and used to produce biodiesel from Kesambi (*Schleichera oleosa l.*) oil (KO). The catalyst was synthesized using a combination of precipitation, impregnation, and gel process. Before being used for transesterification of kesambi oil, NZCA catalyst was characterized using the X-ray diffraction (X-RD), Brunauer-Emmett Teller (BET), and Scanning Electron Microscopy (SEM) methods. The transesterification process was conducted in a glass batch type reactor with refluxed methanol. The effect of loading ZnO (wt.% to alumina), reaction temperature, and amount of catalyst (wt.% to kesambi oil) on the yield of biodiesel were investigated, respectively. The results showed that the catalyst of NZCA was potentially used for transesterification of kesambi oil. The highest biodiesel yield of 89.21% was achieved.

1. Introduction

At present, the world is facing by an energy crisis because so far energy needs have been supplied by fossil fuels. The fact fossil fuel is non-renewable sources, when it used continuously have an impact on the depletion of world crude oil reserves [1]. The other important impacts are the increase in global warming, increasing air pollution and various other environmental problems [2]. To overcome these problems, now researchers are intensively developing alternative energy sourced from renewable materials. Their efforts include the development of clean and environmentally friendly fuels from biomass such as bio-fuels [3]. Biodiesel represents the green alternative to diesel oil among liquid bio-fuels, because it was derived from renewable sources in this case lipid sources (vegetable oils, animal fats and used cooking oil) [4].

The method commonly used for producing of biodiesel is the transesterification reaction of those lipid sources with short-chain alcohols (preferably methanol) with the presence of a homogeneous



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catalyst to form esters and glycerol [5], [6]. This process is most preferred for industrial scale because it's simple, mild temperatures operation, and results in high conversion [3]. Many of catalyst compounds can be used to transesterification reactions, including both basic and acid catalysts in either homogeneous or heterogeneous types. Among them, the homogeneous basic catalyst has been most frequently used so far, because it can offer nearly complete reaction in shorter than 3 h at atmospheric pressure and at mild temperatures (65 °C) [3]. However, these types of catalysts have a sensitive nature against the free fatty acid (FFA) and water content of the feedstock [2]. It is required minimizing the contents both of them in the raw material because they can cause undesirable side reactions, such as soap formation [6], hydrolysis of the final ester and the reaction between catalyst and FFA [3]. These undesired reactions result in a decrease of the conversion, catalyst deactivation, and therefore, they lead to a substantial increase in the purification costs due to the need of refining the raw materials prior to their use in the transesterification processes [3]. It has been reported that 75-90% of the total production cost of biodiesel come from feedstock cost [7], [8].

Thus, to reduce the production cost, the utilization of cheap feedstock is the focus of much research today. Non-edible oil seems to be a promising feedstock for biodiesel production because it is cheaper than edible oils and abundant availability in Indonesia [2], [9]. Non-edible oil has a high fatty acid (FFA) content of about >2.5 wt.%, saponification may occur by the neutralization of the free fatty acids (FFAs) when a heterogeneous or homogeneous alkaline catalysts is used for the transesterification of the non edible oil. Therefore, the application of a heterogeneous acid catalyst (solid acid catalyst) is preferred for biodiesel production because of the high FFA content of the non-edible feedstock [2], [10].

Several solid acid catalyst namely metal oxides from the group of transition metals as well as some from the group of earth metals could be successfully applied as an acid catalyst for production of biodiesel of non-edible and low-grade oil [2]. Zinc and copper that belong to group transition metal were suitable catalyst for biodiesel synthesis biodiesel. Istadi et al. [11] stated that $\text{SO}_4^{2-}\text{ZnO}$ is a promising catalyst for transesterification of soybean oil, with 80.19% yield obtained under mild conditions. Other researchers developed copper doped zinc oxide nano composite (CZO) as a heterogeneous catalyst for transesterification of waste cooking oil [12]. They reported that CZO catalyst was potentially used as a heterogeneous catalyst for biodiesel production from waste cooking oil. Modified zinc oxide was stated as a good catalyst for the transesterification of rapeseed oil due to its high activity and minimal weight loss [11], [13]. Alumina supported zinc oxide catalyst have been develop for transesterification of kesambi oil, and reported that the highest yield of 92.29 % was achieved. So far, there are no earlier studies developing double promoted catalyst for transesterification of low-grade oil. In the next, it is important to explore and develop various non-edible and low-grade oil for producing biodiesel. Moreover, it also needs to develop the appropriate catalyst for transesterifying both kinds of oil.

In this work, we focus on develops nano CuO-ZnO catalyst supported by γ -alumina (NZCA) for transesterifying of kesambi (*Schleichera olesosa L*) oil. Kesambi oil (KO) is potential and promising used as biodiesel feedstock associated with its high of oil content, low price and its abundant availability in Indonesia. In addition, it will not compete with food industrial. Hence, the stability of national food will be safe constantly. The activity of the synthesized NZCA catalyst was observed via transesterification of KO. The effects of several operational parameters include amount of catalyst and reaction temperature on yield of biodiesel were investigated.

2. Materials and Methods

2.1 Materials

Kesambi oil was found from local market at Pasuruan, East Java. Before use, the physical and chemical characteristics of KO were analyzed using several methods based on the procedure described at the previous work [2]. The free fatty acid (FFA) content was analyzed based on American Oil Chemist (AOCS) official Method (Ca 5a-71, 1993). Meanwhile, its density and water content were analyzed based on ISO 662 – 1089. Fatty acid composition of KO was analysed using Gas Chromatography – Mass Spectrophotometer (GC-MS). FAME standards and internal standards of chromatographic grade were obtained from Sigma–Aldrich (Switzerland). A commercial grade of methanol used as a reactant for the transesterification process was also purchased from the domestic market. Merck, Germany provided the analytical grade reagents used for NZCA catalyst preparation including sodium hydroxide, methanol, zinc chloride, sodium carbonate, and gamma alumina. They were used directly without any further purification. Merck, Germany also supplied all standard reagents for gas chromatography analyses.

2.2 Catalyst preparation and characterization

Nano CuO-ZnO (NCZA) catalyst-supported by gamma alumina was prepared via precipitation, impregnation and gel methods. The synthesis of NCZA catalyst started with the preparation of precursor, which in this case, there were two types of precursor including zinc methoxide ($Zn(OCH_3)_2$) and copper methoxide ($Cu(OCH_3)_2$). Zinc methoxide was prepared by reacting 50 ml of 3% sodium hydroxide solution, 25 ml of methanolic zinc chloride solution with 15% loading of ZnO (wt.% to alumina). Copper methoxide was also prepared in the same way using cupric sulfate as precursor with 15% loading of CuO. Both solutions then were precipitated into the dispersion of 5 g $\gamma-Al_2O_3$ in 25 ml distilled water and mixed vigorously for 3 h. The resulted mixture then was dropwise added by fifty ml of 1 mole sodium carbonate and mixed vigorously with a constant speed of magnetic stirrer for 3 h (the temperature and pH were kept constant at 60 °C and 11, respectively). Further, the mixture was evaporated at 80°C while stirring until the gel was formed.

The formed gel was dried at 80° C in an oven for 12 hours. The dried synthesized catalyst was crushed, milled into powder and then calcinated at 500° C in a muffle furnace for 5 h. Subsequently, the catalyst powder was stored in a desiccator equipped with silica gel to avoid contact among catalyst, water and carbon dioxide. Furthermore, four others types catalyst were synthesized which varied of ZnO loading from 20 upto 35 % (wt.% $\gamma-Al_2O_3$) with interval of 5%, meanwhile loading CuO was kept constant at 15% (wt. % to $\gamma-Al_2O_3$) using the same procedure.

Those synthesized catalysts were coded as NZ₁₅C₁₅A, NZ₂₀C₁₅A, NZ₂₅C₁₅A, NZ₃₀C₁₅A, and NZ₃₅C₁₅, respectively. Finally, all types of calcined catalyst were characterized using several methods include x-ray diffraction (X-RD), Brunauer–Emmett–Teller (BET), X-ray fluorescence (XRF), and Scanning Electron Microscopy (SEM) methods. The total specific surface area, pore volume and average pore diameter of the prepared catalysts were measured using the BET method. The XRF method was used to obtain information regarding the composition of the catalyst. Meanwhile, The SEM study gives the morphological characteristics of the catalyst.

2.3 Transesterification process

Before transesterification process, the collected KO was pre-treated by heating and degumming process based on the procedure described at the previous work [2] [5]. First, the collected KO was pour into the 1 l of beaker glass, and then it was heated at 100-105 °C for 30 minutes to remove the excess of water content. The heating process was continued at the same temperature (100-105 °C) for 4 hours to reduce the FFA level. Further, the degumming process was done to remove the gum of the KO. In this study, it was conducted using analytical grade phosphoric acid namely 0.1% (v/wt. of KO). The mixture was stirred at 70 °C for 30 minutes followed by a washing process with distilled water and stirred slowly for 5 minutes. Then, it was poured in the suction flash and left at room

temperature for 48 hours until form the three layers. The oil was in the top layer, followed by the gum in the middle, and water at the bottom. The oil layer was separated as treated oil. Finally, the treated KO was ready for transesterifying into biodiesel.

Transesterification process of Kesambi oil (KO) using NCZA catalyst was conducted by playing conventional methods in batch type reactor consists of three-neck glass, equipped with reflux condenser and magnetic hot plate stirrer. There were two independent variable involved in this work include reaction temperature and amount of catalyst. There were four levels of reaction temperature (50, 60, 70, and 80 °C) and five varied the amount of catalyst from 3 to 7% with an interval of 1%. Meanwhile, the reaction time and molar ratio of oil to methanol were kept constant at 12 h and 1:15, respectively. The influences of independent variables were investigated using one-variable-at-a-time (OVAT) approach [8]. Usually, the experiment was run by varying one factor or variable while keeping the others fixed. The OVAT approach is very simple to implement, also it is very helpful in selecting factors that influence the tested parameters (yield of biodiesel).

The detailed procedure of the transesterification process has been described in the previous work [2]. Methanol, the treated KO, and amount of NZCA were measured and introduced into the reactor. Turn on the hot plate, wait a while until achieving the desired reaction temperature. Subsequently, the mixture was stirred vigorously at a constant speed using a magnetic stirrer. After reaching the desired duration time, the reactor was cold down at room temperature and the reaction mixtures taken out and then filtered to separate the catalyst from the liquid phase. The liquid phase was poured into a separation funnel. The glycerine was decanted, and then the excess methanol was recovered using a rotary evaporator. Biodiesel concentration was analyzed by a gas chromatograph GC-14B (model Shimadzu) equipped with a flame ionization detector and a capillary column HP-Innowax (30 m × id 0.25 mm, 0.25 μm). Helium was used as the carrier gas throughout the whole experiment. Biodiesel analyses can be used to calculate the yield of biodiesel (%) defined as equation (1) [1].

$$\text{Yield of biodiesel (\%)} = \frac{w_{of ab}}{w_{of oil}} \times 100\% \quad (1)$$

Where, $w_{of ab}$ means weight of actual biodiesel was calculated from weight of biodiesel produced (mg) in the experiment multiple by concentration of FAME (wt.%) in the sample. Meanwhile, $W_{of oil}$ is weight of oil (mg) used in the experiment.

3. Results and Discussion

3.1 Characterization properties and fatty acid composition of KO

The characteristics of KO were presented in Table 1. The acid value and the iodine value measured in the collected KO was 64.77 mg KOH/g and 149.77 mg I₂/g, where this value significantly difference compared with Silitonga et al. [14] which is 20.6 mg KOH/g and 92.6 mg I₂/g, respectively. This shows that kesambi oil has a double bond that is quite large compared to other vegetable oils, indicate that KO as high-unsaturated acid. Meanwhile, the free fatty acid (FFA) and water content of KO was higher than previous results [14], namely 29.56 and 0.19% compared to 20.6 and 0.0005%, respectively.

The high water content of KO is probably caused by an enzymatic process of lipase in the seed cell and produce water as a side product [15]. Water content is an important parameter in determining oil quality. Water that is present in the oil will result in the hydrolysis of triglycerides into fatty acids and glycerol, thereby increasing the levels of free fatty acids (FFA). The high content of free fatty acids will reduce the yield of biodiesel. The method of storing oil also affects the water content and acid number of the oil. Although acid solid catalyst more insensitive to FFA compare with base heterogeneous catalyst, FFA content of KO (29.56%) is too high, it still needs to reduce. Therefore, kesambi oil must be purified before being transesterified, otherwise resulting in a decrease in the yield

of biodiesel. After purification process, the yellowish colour free gum of KO was obtained with 0.034% of water content.

Table 1. Characterization results of kesambi oil

KO properties	Value	Unit	Methods
Acid value	64.77	mg KOH/gr KO	AOCS Official Method Cd 3d-63, 2012
Free fatty acid (FFA)	29.56	%.	AOCS Official Method Cc 5a-40, 2012
Saponification value	181.62	mg KOH/gr KO	AOCS Official Method Cd 3-25, 2012
Iodin value	149.77	mg I ₂ /gr KO	AOCS Official Method Cd 1-25, 2012
Density	0.8802	gr/cm ³	gravimetric
Water content	0,19	%	gravimetric

Table 2 showed the fatty acid composition of KO and compared with the others. It shows that unsaturated fatty acids are the major component of KO, which is 91.08%. The major compositions of KO are linolelaidic acid and eicosenoic acid namely 50.05 and 28.97%, respectively. Palmitic acid and oleic acid are in the third and fourth order, which is 7.42 and 2.59%. These results are consistent with previous studies [16], but differ significantly from the results presented by Silitonga et al. [14] and Sudrajat [15]. The main components according to them are oleic acid (51.49 and 49.29%) followed by Arachidic acid (27.21 and 29.24%).

Table 2. Fatty acid composition of KO compared with other *Schleichera oleosa l.*

Fatty acid	Structure	(wt. %)			
		KO	Kesambi Oil (Sudajat, 2010)	<i>S. oleosa</i> oil (Silitonga, 2015)	Kusum oil Rathod (2013)
Myristic acid	C14:0	0.01	0.1	0.09	0.01
Palmitic acid	C16:0	7.42	7.58	7.83	7.59
Palmitoleic acid	C16:1 n-7	1.90	2.83	2.88	1.80
Stearic	C18:0	-	5.21	5.81	-
Oleic acid	C18:1 n-9 <i>Cis</i>	2.59	49.29	51.49	2.83
Linolelaidic acid	C18:2 n-6	50.05	-	-	49.69
Linoleic acid	C18:2 n-6 <i>Cis</i>	5.35	5.53	5.51	5.56
alpha-Linolenic acid	C18:3 n-3	0.56	0.22	0.27	0.26
Arachidic acid	C20:0	-	29.24	27.21	-
Eicosenoic acid	C20:1 n-9	28.97	-	-	29.54
Eicosadienoic Acid	C20:2 n-6	0.29	-	-	0.24
Heneicosanoic Acid	C21:0	0.06	-	-	0.04
Behenic Acid	C22:0	1.21	-	-	1.14
Erucic acid	C22:1	1.33	-	-	1.22
Lignoceric Acid	C24:0	0.02	-	-	0.03
Docosaheaxaenoic Acid	C22:6	0.04	-	-	0.02

3.2 Characterization of NZCA

The crystallographic structure of synthesized catalyst was being verified using X-ray diffraction (XRD). The patterns of prepared NZCA catalyst performed by Panalytical x'Pert Pro MPD were depicted in figure 1. Figure 1 (a)-(e) shows the X-RD pattern of C₁₅Z₁₅A, NZ₂₀C₁₅A, NZ₂₅C₁₅A, NZ₃₀C₁₅A, and NZ₃₅C₁₅, respectively. A rectangular shape and monoclinic structure of CuO was

clearly shown. The peaks of CuO were registered at $2\theta=25.49^\circ$, 31.78° , 35.51° , 38.73° , and 48.80° . The diffraction peaks are in a good agreement with the standard pattern of CuO (JCPDS card NO. 050661). Mahmoodi et al. [17] also reported the similar result. The low and a wide peaks at $2\theta=45.79^\circ$, 66.40° and 69.22° assigned to amorphous Al_2O_3 support. The others peaks also appeared at $2\theta=25.49^\circ$, 31.78° , 35.51° , 38.73° , 48.80° , 61.62° , 63.90° , 66.27° , and 68.07° were assigned as hexagonal wurtzite ZnO. The intensities and position of the peaks are in good agreement with standard of hexagonal wurtzite ZnO (JCPDS Card No. 36-1451). Mahmoodi et al. [17] was reported the similar results. The low and wide peaks of amorphous Al_2O_3 support still appear but slightly shifted into $2\theta=34.01^\circ$, 46.36° and 58.32° . It was clearly seen, that there are two series of diffraction peaks appeared corresponding to hexagonal wurtzite ZnO and monoclinic CuO. In addition, the diffraction peaks of Al_2O_3 are still present and virtually unchanged against CuO and ZnO loading. This shows despite the 2-phase crystals of CuO and ZnO, alumina remains in the form of amorphous structures, for thereby generating catalysts with a high surface area that were necessary for catalyzes. The similar statement also reported by previous researchers [4], [18]

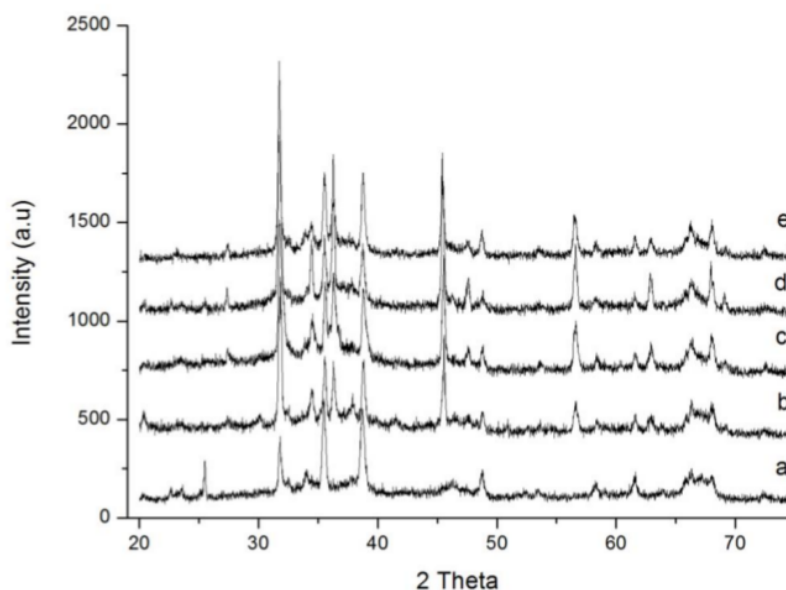


Figure 1. X-RD pattern of NZCA catalysts, (a) $NZ_{15}C_{15}A$; (b) $NZ_{20}C_{15}A$, (c) $NZ_{25}C_{15}A$, (d) $NZ_{30}C_{15}A$, (e) $NZ_{35}C_{15}A$

The BET specific surface area of the prepared NZCA catalysts was shown in table 3. There were five types of catalyst have been synthesized include $NZ_{15}C_{15}A$, $NZ_{20}C_{15}A$, $NZ_{25}C_{15}A$, $NZ_{30}C_{15}A$, and $NZ_{35}C_{15}A$. It shows that the greater loading ZnO the greater surface area of the catalyst. It was possibly due to the catalyst in nano size, part of them well dispersed in the pore of alumina as a support and the rest remain in the surface of catalyst as site active. Therefore, the greater the loading ZnO the more nano ZnO particle were remaining in the surface and result in the more of the active site will be.

Table 3. BET surface area of synthesized catalyst

Type of catalyst	$NZ_{15}C_{15}A$	$NZ_{20}C_{15}A$	$NZ_{25}C_{15}A$	$NZ_{30}C_{15}A$	$NZ_{35}C_{15}A$
BET surface area (m^2/g)	316.54	328.49	369.31	377.16	433.86

Scanning Electron microscopy (SEM) has been a primary method and as intensively used for determining morphology or the particle shape and appropriate size distribution of a solid particle include the catalyst. Figure 2 saws the SEM image of a prepared NZCA catalyst. The synthesized alumina supported-zinc oxide- copper oxide catalyst for all types of catalyst (figure a-e) had a hierarchical 3D morphology composed of flower-like ZnO microstructure integrated with of CuO in rectangular-shape monoclinic structure. The size distribution both of them between are 0.2-1 μ m and 2-10 μ m, respectively. From the images, it was clear that the NZCA catalysts were a nanosize particle. The SEM profile of the synthesized NCZA catalyst was in good agreement with the X-RD pattern of NZCA catalysts as shown in figure 1 that there are two series of diffraction peaks hexagonal wurtzite ZnO and monoclinic CuO.

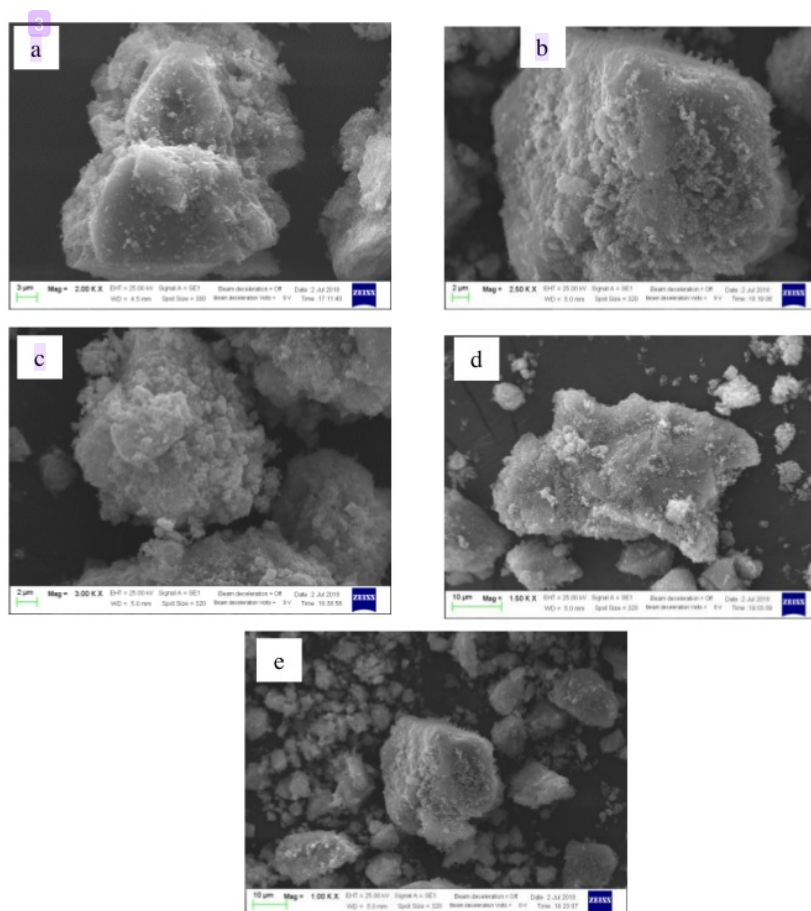


Figure 2. SEM image of NZCA catalyst, (a) $Z_{15}C_{15}A$; (b) $Z_{20}C_{15}A$, (c) $Z_{25}C_{15}A$, $Z_{25}C_{15}A$ (d) $Z_{30}C_{15}A$, (e) $Z_{35}C_{15}A$

3.3 Effect of operational parameter on yield of biodiesel

Several operational parameters affect the transesterification process such as, the reaction temperature, the reaction time, molar ratio of oil to methanol, the speed of mixing, and many others. In addition, the

type triglyceride, the type of catalyst used, catalyst amount and the method of catalyst preparation were also very influential on the transesterification process. Therefore, to get an efficient process and high biodiesel yield, those parameters need to be intensively investigated. In this work, we focused on the influence of the catalyst amount used and the reaction temperature on yield of biodiesel.

FFA and moisture content are the two important parameters influencing the transesterification process of vegetable oil [2]. The availability of water in the feedstock will accelerate the hydrolysis reaction and simultaneously reduce the amount of ester formation [19]. To achieve 90% yield of biodiesel, then water content of triglyceride that used in the transesterification process not more than 0.5% [20]. Moreover, theoretically the higher free fatty acid contents would lead to formation of soap and water. If free fatty acid content more than 3%, the homogeneous base catalyst is not suitable for the transesterification reaction [2], [20]. Therefore, in this work, NZCA catalyst was used to substitute homogeneous catalyst for transesterification process. The activity of NZCA will be investigated through simultaneous reaction of esterification and transesterification of kesambi oil, which has high FFA and water content. Based on the characteristic of synthesized catalyst, $NZ_{35}C_{15}$ was selected for investigating the effect of the operational parameter on the yield of biodiesel in the further experiment, due to it has the highest surface area compared with the others.

3.3.1 Effect of catalyst amount on yield of biodiesel

The investigation of the influence of catalyst amount on the yield of biodiesel was carried out via the OVAT approach. The experiments were performed in varied catalyst amount of 3-7% with range of 1% (wt.% to KO) under constant stirring speed at reaction temperature, reaction time and molar ratio of KO to oil at 70 °C, 12 h, and 1: 15, respectively. Figure 3 shows the effect of catalyst amount on yield of biodiesel. As depicted by figure 3 the amount of catalyst was significantly influence on yield of biodiesel. Yield of biodiesel increases with increasing the amount of catalyst. The increase in biodiesel yield with the increasing of catalyst amount could be due to the more of active site available on the surface of NZCA catalyst. Indeed, the more presence active site on the surface of catalyst the faster rate reaction will be. Yield of biodiesel linearly increase along with the increasing of catalyst amount from 3 to 5%. With the increasing amount of catalyst from 3 into 4% could increase the yield of biodiesel from 80.25 to 84.48%. The biodiesel yield also gradually increases from 84.48 to 88.66% at the increasing amount of catalyst from 4 to 5%.

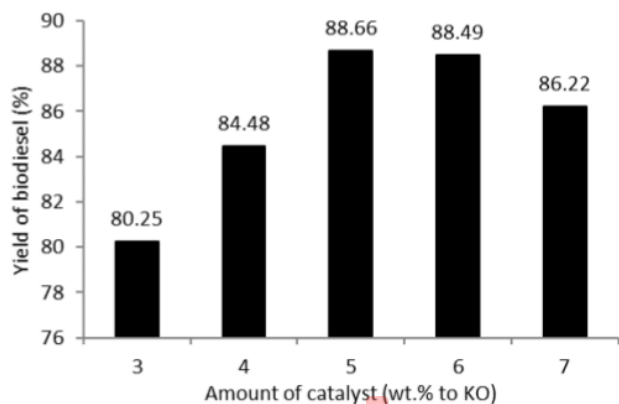


Figure 3. Effect amount of catalyst (wt.% to KO) on yield of biodiesel (%) at reaction temperature 70°C, reaction time 12 h and molar ratio of oil to methanol 1:15

In contrary, yields of biodiesel slightly decrease at catalyst amount loading of 6%. Even, at loading 7% amount of catalyst, it was significantly decreased to 86.22%. It is possibly; due to beyond 5% amount of catalyst the mixture being viscous and inhibit the diffusion among the reactants and catalyst, and finally it can inhibit the speed of the transesterification reaction [4]. It is strongly evidence that the presence of catalyst significantly affected the reaction rate of transesterification [2]. In this work, the maximum biodiesel yield of 88.66% was achieved at 5% amount of NZCA catalyst at fixed others operation parameter. Therefore, the catalyst amount of 5% was selected for investigating the effect of reaction temperature on yield of biodiesel.

3.3.2 Effect of reaction temperature on yield of biodiesel

Theoretically, the reaction temperature is strongly influence the rate of transesterification reaction, because the reaction temperature significantly influenced the rate constant of the transesterification reaction. According to Arrhenius law the rate constant of reaction increased with the increase of reaction temperature. The higher the rate constant of the reaction, the faster the rate of reaction, because of the reaction rate directly proportional to the rate constant of reaction [5]. The impact of reaction temperature on yield of biodiesel on transesterification of KO using NZCA catalyst was studied also using OVAT approach. The reaction temperatures were varied from 50-80 °C with interval of 10 °C under constant stirring speed. Meanwhile, the others conditions such as reaction time, molar ratio of KO to methanol, amount of catalyst were kept constant, at 12 h, 1:15, and 5% (wt. % to KO).

Fig. 4 shows the effects of reaction temperature on biodiesel yield. The reaction temperature significantly influences the transesterification reaction, where the biodiesel yield increased with an increase in reaction temperature. These results are in accordance with Arrhenius law, which states that the intrinsic rate constants are a function of reaction temperature [4]. A low biodiesel yield of 51.27% was achieved at the low reaction temperature of 50 °C. At higher temperatures (60, 70 and 80 °C), the obtained yield is higher than that the low temperature. It can be possible because the boiling point of methanol is 64.9 °C, so the kinetic energy of the system increased, eventually enhancing the frequency factor. The increased frequency factor resulted in an increased the rate constant of reaction [5]. Furthermore, the increasing of kinetic energy also enhances the mass transfer rate between KO, methanol and CZCA catalyst. Finally, both of them can increase the yield of biodiesel [4].

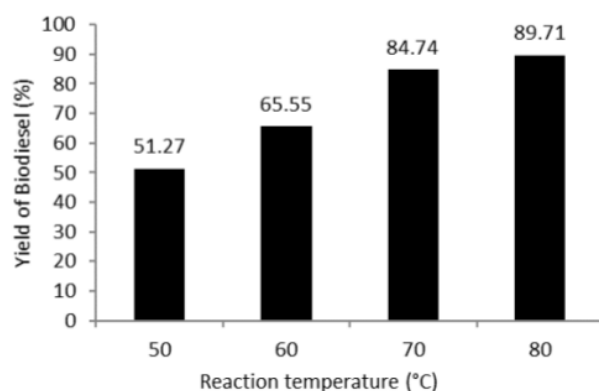


Figure 4. Effect of reaction temperature on yield of biodiesel (%) reaction time 12 h, molar ratio of oil to methanol 1:15 and 5% of catalyst amount.

In this work, the highest biodiesel yield of 89.71% was achieved at 80 °C, 12 h of reaction time, 5% catalyst amount on transesterification of Kesambi oil using NZCA catalyst. This result was lower

than that of Silitonga et al. [14]. They obtained a maximum yield of 96% at 55 °C with a molar ratio of oil/ methanol, KOH concentration and reaction time of 1: 8, 1%, and 90 minutes, respectively. It should be noted that Silitonga et al. [14] using a homogeneous base catalyst reaction. As a fact, it offers a nearly complete reaction. However, as explained in the introduction section, that homogeneous catalysts have many disadvantages such as the difficulty of separating the catalyst from the product and resulting in considerable alkaline liquid waste. Both require more serious handling with complex processes, so that production costs become more expensive. Moreover, they use the two-step process include esterification of FFA followed by transesterification of TG. In addition, the FFA content of their feedstock (*S. oleosa l. oil*) much lower than that of KO oil. In this work, we only use one stage process even though the FFA content of KO are relatively high compared to Silitonga's feedstock. It could be possible, due to the active site of Lewis acid of Zn^{+2} and Cu^{+2} which insensitive against FFA hence the esterification and transesterification work simultaneously.

4. Conclusion

In this study, five types of a novel nano solid catalyst NZCA ($NZ_{15}C_{15}A$, $NZ_{20}C_{15}A$, $NZ_{25}C_{15}A$, $NZ_{30}C_{15}A$, and $NZ_{35}C_{15}A$) have been synthesized successfully using the combination of precipitation, impregnation and gel methods. The synthesized NZCA catalysts have been characterize using X-RD, BET and SEM methods. The synthesized NZCA catalyst had a hierarchical 3D morphology composed of flower-like ZnO microstructure integrated with a rectangular shape CuO, with size distribution between 0.2-1 μ m and surface area in the range of 316.537- 433.863 m²/g. The characteristic CZA catalyst shows that the CZA catalyst is a nanosize particle. The activity of the highest surface area NZCA catalyst ($NZ_{35}C_{15}A$) has been tested through transesterification of kesambi oil with methanol. The maximum yield of 89.71% was achieved at 80 °C with molar ratio of KO/methanol, reaction time, and catalyst amount of 1:15, 12 h, and 5%, respectively. It proved that the possibility of non-edible kesambi oil as a promising feedstock for the production of biodiesel using a novel NZCA solid catalyst, and could be used as a potential benign alternative fuel. The further study of optimizing the parameters that influence the transesterification process is needed to be done to enhance the yield of biodiesel.

Acknowledgments

The authors would like grateful to Directorate of Research and Community Services, Directorate General of higher education, the Ministry of Research Technology and Higher Education Republic Indonesia, for the financial support through the Competence Based research grant on fiscal year of 2019 by Contract No. 011/SP2H/LT/MULTI/L7/2019.

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