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Original Research Article

Determination of Optimum Conditions for Synthesis of Methyl Ester from Bleached Crude Palm Oil Using Sn-Zeolite and Red Mud Catalysts

Esi Amelyanti[1], Thamrin Usman[1]*, Winda Rahmalia[1]
[1]Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Tanjungpura, Pontianak 78124, West Kalimantan, Indonesia
*Corresponding Author, email: tamrin_usan@untan.ac.id

Abstract
Methyl esters synthesis from bleached crude palm oil (BCPO) containing 0.36 and 20.86% of free fatty acids using Sn-zeolite and red mud has been done. This study aims to determine the esterification, transesterification, and transesterification-esterification simultaneous reactions optimum conditions when using Sn-zeolite, red mud, and Sn-zeolite-red mud mixture catalysts. The X-ray diffraction and Fourier transform infrared analysis results show that Sn has been impregnated on zeolite, indicated by cassiterite and Sn-O-Sn vibrational peaks in Sn-zeolite. The main component of red mud is $NaCO_3$, indicated by analcite and carbonate peaks. Thin-layer chromatography results in the transesterification showed that red mud catalyst could totally convert triglycerides from BCPO to methyl ester when 5% catalyst, 3 hours, and CPO:methanol mole ratio 1:20 were used. In esterification, Sn-zeolite can synthesize methyl ester from low-quality CPO when using CPO:methanol mole ratio 1:20 for 3 hours, however, the conversion was not total. In the transesterification-esterification simultaneous, the conversion was also not total which the best reaction conditions at mixing Sn-zeolite:red mud 1.5:1 (w/w), 7% catalyst, and CPO:methanol mole ratio 1:20 for 3 hours. This study shows that esterification and transesterification processes can be carried out simultaneously at a particular mass ratio of Sn-zeolite and red mud.

Keywords: Biodiesel; bleached crude palm oil; methyl aster; red mud; Sn-zeolite

1. Introduction

The increase in energy demand, especially diesel engine fuel, has occurred since the mid-1980s due to the increasing number of industries, transportation, and Diesel Power Plant Centers (Putri & Edy, 2020). Environmentally friendly renewable energy, such as biodiesel, can be an alternative to conventional diesel oil (Hazrat et al., 2021). Biodiesel or methyl ester has also been designated a fuel with lower exhaust emissions (Peter et al., 2021). Generally, biodiesel production is produced through esterification and transesterification reactions between methanol and fatty acid using chemical and biological catalysts (Nenobahan et al., 2020). Biodiesel consists of mono-alkyl esters derived from long-chain fatty acids originating from plants. One of the potential natural resources for the development of biodiesel in Indonesia is crude palm oil (CPO) (dos Santos et al., 2018; Usman et al., 2019).

CPO has the main content of triglycerides, diglycerides and monoglycerides. Minor components of CPO consist of carotenoids, tocopherols, tocotrienols, sterol sterols, phospholipids, glycolipids, terpenes, and aliphatic groups, as well as other trace elements. There are also impurities in CPO, namely free fatty acids (FFA). The amount of FFA in a CPO determines the quality of the CPO. Generally, two

reaction steps could be used to synthesize biodiesel from CPO based on differences in FFA levels. These reactions include a transesterification reaction using an alkaline catalyst for CPO with an FFA of less than 5% and an esterification reaction using an acid catalyst for CPO with an FFA of more than 5% (dos Santos et al., 2018; Peter et al., 2021). In addition, esterification and transesterification can be carried out simultaneously using a catalyst that has both acidic and basic sites (Usman et al., 2019).

The conventional catalyst commonly used to produce methyl esters is homogeneous (one phase and soluble in methanol). Homogeneous catalysts have several advantages, including reacting quickly, high conversion values, and using few catalysts (Manuale et al., 2015). However, the resulting methyl ester is challenging to separate from the catalyst, so the catalyst cannot be reused and produces large amounts of water waste. Heterogeneous catalysts have many advantages, including easier separation of products and catalysts, reusability, reduced amount of wastewater produced, and less sensitivity to water in raw materials (Tang et al., 2018; Gupta & Singh, 2023). Heterogeneous catalysts in the methyl ester transesterification process that have been used are MgO, SrO, Zeolite, ZnO, TiO_2, CaO, $CaCO_3$, and Al_2O_3. Alkali metal oxides such as MgO, CaO, and SrO have high activity for use in the transesterification process (Wendi & Taslim, 2015).

Sn metal has the potential to be used in the development of heterogeneous catalysts because it is a Lewis acid which is more significant when compared to other transition metals, including zinc (Zn), lead (Pb), and mercury (Hg) (Alimuddin et al., 2017). Yustira et al. (2015) reported that the Sn-zeolite catalyst in synthesizing methyl esters with palm oil sludge as raw materials were dominated by mordenite and quartz in the presence of Bronsted and Lewis acid sites. Because of its acidity, Sn-Zeolite can be used as a catalyst for esterification reactions. Zeolite has been used as ion exchange and molecular sieves in the separation and removal of gasses and solvents. They also have the ability to act as a catalyst for chemical reactions which take place within the internal cavities (Manadee et al., 2017).

Red mud is a residue or waste material from bauxite processing for alumina production. It has a pH range of around 11-13 and (Ramadhani & Dian, 2018). Liu et al. (2013) reported that biodiesel production from vegetable oil using a red mud catalyst could produce biodiesel exceeding 94% for 3 hours. The advantages of using a red mud catalyst include low cost and environmental friendliness because it can significantly reduce environmental waste (Zhang et al., 2016). In this research, Sn-zeolite and red mud catalysts were prepared and mixed with various compositions, which were used to synthesize methyl ester from CPO with ALB <5% and ALB >5% by transesterification, esterification, and transesterification-esterification (simultaneously). Mixing the Sn-zeolite and red mud catalyst aims to obtain a catalyst with two active sites of acid and alkali to catalyze simultaneous esterification and transesterification reactions.

Hence, this study aims to determine the esterification, transesterification, and transesterification-esterification simultaneous reactions optimum conditions when using Sn-zeolite, red mud, and Sn-zeolite-red mud mixture catalysts. The catalysts were analyzed using X-ray diffraction (XRD), and Fourier transforms infrared (FTIR). The formation of methyl ester from the reaction process was observed using thin-layer chromatography (TLC). The reaction parameters that have been studied were the ratio of Sn-zeolite and red mud (w/w), catalyst concentration (% w/w), and the mole ratio of CPO:methanol to produce the best methyl ester conversion. Before making biodiesel, CPO was bleached to reduce the concentration of minor components such as carotenoids, tocopherols, and phospholipids, which may interfere with the reaction process.

2. Methods

2.1 Materials

The materials used in this study include distilled water (H_2O), hydrochloric acid (HCl), CPO with an FFA content of 20.86% obtained from PT. Pundi Lahan Khatulistiwa (PLK) Ambawang, CPO with FFA content of 0.36%, dichloromethane (CH_2Cl_2), ethanol (C_2H_5OH) p.a, phenolphthalein indicator, potassium hydroxide (KOH), Whatman filter paper, anhydrous magnesium sulfate ($MgSO_4$), methanol

(CH_3OH), sodium chloride (NaCl), silica gel 60 F_{254} plate thin layer chromatography (TLC), red mud obtained from PT. Indonesia Chemical Alumina (ICA) Tayan, cyclohexane (C_6H_{12}), tin chloride ($SnCl_2$), zeolite. The equipment used includes a 100-mesh sieve, 50 mL burette, desiccator, Erlenmeyer, hot plate, porcelain crucible, 250 mL three-neck flask, magnetic stirrer, analytical balance, oven, glassware, pH meter, reflux set, thermometer, x-ray diffraction (XRD) Philips Xpert MPD, and SHIMADZU Fourier transform infrared (FTIR).

2.2 Preparation of Catalyst

a. Red mud

Red mud sample preparation was carried out by heating it in an oven at 105ºC for 4 hours. Dry red mud was crushed until smooth and sieved through a 100-mesh sieve. In the discussion section, the red mud that passes through the 100-mesh sieve is called red mud A. Red mud A was then calcined at 200°C. The calcinated product is called red mud B (Liu et al., 2013). Red mud A and B were then characterized using FTIR and XRD to determine the effect of preparation temperature.

b. Sn-zeolite

Zeolite was washed using distilled water and dried at 105°C for 4 hours. Zeolite was crushed and sieved with a 100-mesh sieve. Sn-zeolite was synthesized by impregnating Sn on zeolite at a mass ratio of 4:1 using a two-neck flask for 6 hours. The mixture was separated using vacuum filtration and dried at 105°C for 4 hours. The product was calcined at 450°C for 4 hours (Kusuma et al., 2011). Zeolite and Sn-zeolite was then analyzed using FTIR and XRD.

2.3 Bleaching of Crude Palm Oil

There are two samples of CPO. They are good and low-quality CPOs. Each CPO was bleached using bleaching earth (BE) at a mass ratio of 1:20. The mixtures were heated at 65°C and stirred thoroughly. The mixture of CPO and BE was left for 24 hours to settle. After filtration, filtrate was heated at 105°C for 4 hours, and the FFA value was determined.

2.4 Synthesis of Methyl Ester from Crude Palm Oil

a. Transesterification from good quality CPO (FFA = 0.36%) using red mud catalyst.

Methyl ester synthesis was carried out under reaction conditions including 5% catalyst concentration, 3 hours, and variation of CPO and methanol mole ratio of 1:10, 1:15, and 1:20. The reaction was followed by TLC technique using dichloromethane and cyclohexane eluents with a volume ratio of 1:2.

b. Esterification from low quality CPO (FFA = 20.86%) using Sn-zeolite catalysts

CPO that has been bleached and synthesized under reaction conditions including 5% catalyst concentration, 3 hours, and variation of mole ratio of CPO and methanol conducted at 1:10, 1:15, and 1:20. The reaction was followed by TLC technique using dichloromethane and cyclohexane eluents with a volume ratio of 1:2.

c. Simultaneously reaction from low-quality CPO using Sn-zeolite and red mud catalysts

Methyl ester synthesis was carried out simultaneously and gradually by making conditions (catalyst mass ratio, catalyst concentration (%w/w), and the CPO to methanol mole ratio. The best methyl ester conversion result was then determined as the best reaction condition.

Determination of the optimum mass ratio of Sn-zeolite and red mud

Biodiesel synthesis was carried out by mixing low-quality CPO and methanol in a ratio mol of 1:15. Next, Sn-zeolite and red mud catalysts were added with a mass ratio variation of 2:1, 1.5:1, 1:1, and 1:1.5 at 5% of the mass of low-quality CPO, then heated at 65ºC and stirred magnetically for 4 hours. The reaction was followed by the TLC technique using dichloromethane and cyclohexane eluents with a volume ratio of 1:2.

Determination of the optimum catalyst concentration (%)

The mass ratio of the Sn-zeolite and red mud mixture used was the optimum mass ratio obtained from the previous stage, the mole ratio of CPO and methanol was 1:15 for 4 hours, and the catalyst concentration varied from 3, 5, 7, and 10% of the mass of CPO and methanol. The reaction was followed by the TLC technique using dichloromethane and cyclohexane eluents with a volume ratio of 1:2.

Determination of sample and methanol ratio

The mass ratio of the Sn-zeolite-red mud mixture, and catalyst concentration used was the optimum mass ratio and catalyst concentration obtained from the previous stage with a time of 4 hours, and variations in the mole ratio of CPO and methanol were carried out at 1:10, 1:12, 1:15, and 1:20. The reaction was followed by the TLC technique using dichloromethane and cyclohexane eluents with a volume ratio of 1:2.

d. Separation product

The solid phase (catalyst) and the liquid phase (residual methanol, residual CPO, methyl ester, and glycerol) were separated using centrifugation at 3500 rpm, followed by liquid-liquid separation using a separating funnel until the top and bottom layers were obtained and separated. The top layer phases were analyzed using TLC and determined the FFA value.

3. Result and Discussion

3.1 Characteristic of Catalysts

XRD analysis

According to Rianto et al. (2012), the position of the diffraction angle (2θ) and the distance between planes (d) describe the type of crystal, while the relative intensity (%) indicates crystallinity. This qualitative analysis is based on comparing the sample diffractogram with the standard diffractogram to obtain information about the mineral type of the sample. **Figure 1** presents the diffractograms of zeolite, Sn-zeolite, red mud A, and red mud B. Based on the diffraction angle position (2θ) of the zeolite diffractogram, it is known that the dominant mineral types in the prepared zeolite are modernite and quartz. This can be seen from the high intensity of typical modernite peaks, especially at 2θ = 13.34, 25.52, and 27.57°. According to Dubidin et al. (1968), the mineral mordenite has typical peaks at 2θ = 22.32, 25.80, and 27.77°. Mordenite zeolite has a ratio of Si/Al = 5 and is very stable to acids and heat (Lestari, 2010).

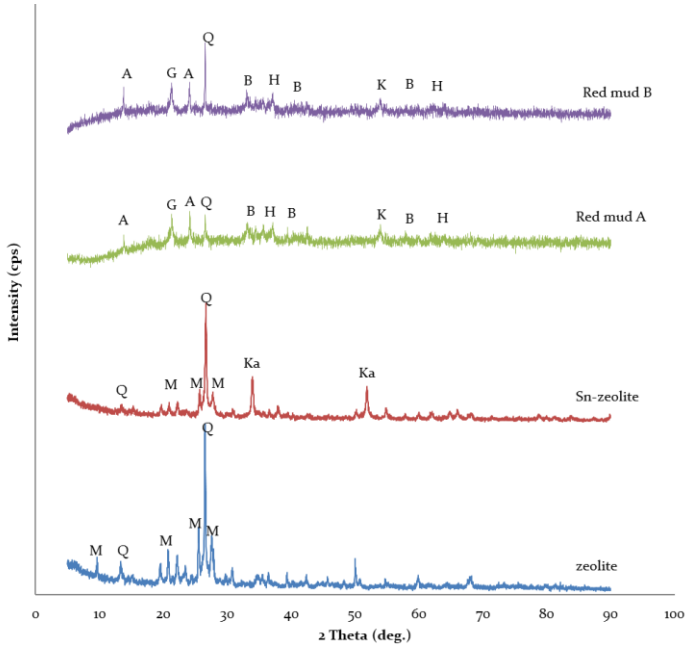

Figure 1. Diffractograms of zeolite; Sn-zeolite; *red mud* A; and *red mud* B

A	= analsite (Na_2O)	K	= causite (Ca_2O)
B	= boehmite (γ-AlO(OH)	Ka	= cassiterite (SnO_2)
G	= ghibsite ($Al(OH)_3$)	M	= mordenite ($K_{2.8}Na_2Ca_2$)($Al_{8.8}Si_{39.2}O_{96}$)
H	= hematite (Fe_2O_3)	Q	= quarzt (SiO_2)

Modernite minerals have components such as potassium, sodium, calcium, aluminum, silicate, hydrogen, and oxygen with the chemical formula ($K_{2.8}Na_2Ca_2$) ($Al_{8.8}Si_{39.2}O_{96}$)(H_2O)$_{34}$ and have pores with a diameter size of 0.65 x 0.70 nm (Korkunaet et al., 2006). The presence of quartz minerals consisting of SiO_2 is characterized by the appearance of peaks with 100% intensity at 2θ 20.79 and 26.51° as in the results of Morris et al. (1981) with peaks at 2θ 20.85 and 26.65°. SnO_2 crystals appeared peaks at 2θ 26.65, 33.90 and 51.83°. These results are in line with the research of Majumder (2009), who reported SnO_2 appeared at 2θ 26.61, 33.89, 51.79, and 61.87°. The 2θ angle of XRD of the Sn-zeolite catalyst has appeared as mineral cassiterite (SnO_2) (Suharyanto et al., 2016). This shows that Sn metal has entered into the zeolite pore, which causes the disappearance and appearance of a new 2θ angle. Alumina and silica that bind the same O atom result in Al being negatively charged. The negatively charged Al in zeolite and supported by the many pores in the mordenite framework, allows the presence of cations such as sodium (Na^+) and calcium (Ca^{2+}) as well as water molecules (H_2O). The mordenite mineral become a site for cation exchange in zeolites.

In this research, after the calcination, the red mud had a pH of 12.5. The XRD patterns between red mud A and B are not much different. Based on the diffraction angle position (2θ) of the red mud B diffractogram, it is known that the main mineral phases in the red mud from the Bayer process consist of analcite ($NaAlSi_3O_8$) at 2θ 13.79 and 24.10; hematite (Fe_2O_3) at 2θ 40.50 and 63.97°; gibbsite ($Al(OH)_3$) at 2θ 24.13 and boehmite (γ-AlO(OH) at 2θ 18.03, 33.12, 35.62, and 57.72°; calcite (CaO_2) at 2θ 53.97°, quartz (SiO_2) at 2θ 21.32 and 26.52°. This result is consistent with the results of Liu et al., 2017 and Liang et al. (2014), who reported the results of XRD analysis result for red mud with peaks of analcite at 2θ 13 and 24°; hematite at 2θ 40, 47, 58, and 64°; gibbsite at 2θ 20 and 24°; boehmite at 2θ 18, 33, 45, and 58°; quartz 2θ 21, 26, and 50°.

FTIR Analysis

The FTIR spectra in **Figure 2** show some typical absorption peaks for zeolites, including pore opening peaks in the 420-300 region at 372.26 and 395.41 cm^{-1}, Si-O or Al-O bending vibrations in the 500-420 cm^{-1} region at 435.91 cm^{-1}, symmetrical Si-O-Si or Al-O-Al stretching vibration in the 820-750 cm^{-1} region at 796.60 cm^{-1}, symmetric Si-O-Al stretching vibration in the 1150-1050 region at 1041.56 cm^{-1}, O-H group bending vibration at 1700-1500 cm^{-1} region at 1641.42 cm^{-1}, the vibration of Si-OH stretching in the ~3400 cm^{-1} region at 3446.79 cm^{-1} (Byrappa & Suresh, 2007), H-OH stretching vibration in the 3570-3200 cm^{-1} region (Coates, 2000) at 3577.95 cm^{-1}.

The Sn-zeolite catalyst shows several absorption peaks, including Si-O or Al-O bending vibrational groups in the 500-420 cm^{-1} region (Byrappa & Suresh, 2007) at 435.91 and 459.06 cm^{-1}, Sn-O-Sn vibrations in the 750-500 cm^{-1} region (Ocana et al., 1995) at 576.72, 545.85, 624.94, 694.37, and 717.52 cm^{-1}. FTIR analysis results indicate that Sn in oxide form has been formed at 450°C calcination and act as a Lewis acid catalyst during synthesis. There are symmetrical O-Si-O or O-Al-O stretching vibration in the 820-750 cm^{-1} region (Byrappa & Suresh, 2007) at 796.60 cm^{-1}, asymmetric Si-O-Al stretching vibration at 1150-1050 cm^{-1} region (Byrappa & Suresh, 2007) at 1041 cm^{-1}, Si-O-H asymmetric stretching vibration in 1200-1100 cm^{-1} region (Robbiola et al., 2008) at 1641.42 cm^{-1}, Si-OH stretching vibration in the ~3400 cm^{-1} (Byrappa & Suresh, 2007) at 3446.79 cm^{-1}. Silanol groups (Si-OH) are hydrophilic so that some of the water formed can be adsorbed (Adhani et al., 2016), in this case, on zeolites and red mud.

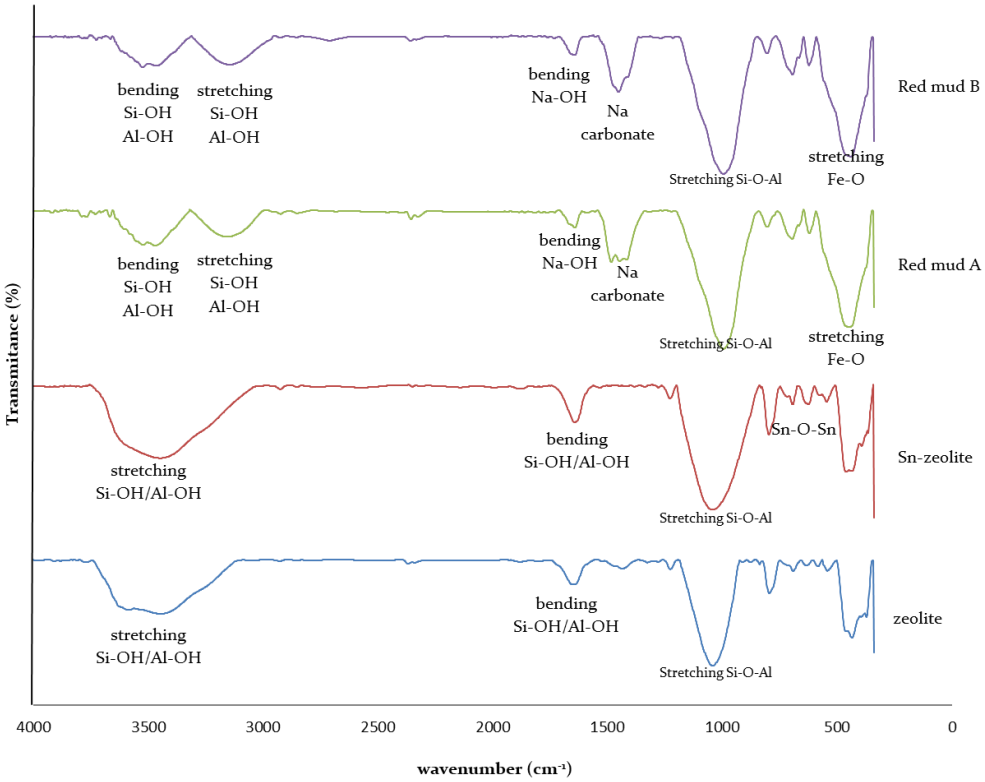

Figure 2. Spectra FTIR of zeolite; Sn-zeolite; red mud A; dan red mud B

The red mud A shows several absorption peaks, including the Fe-O stretching vibration group in the 500-400 cm^{-1} region (Bernes et al., 1999) at 443.63 cm^{-1}, cyclic vibration of Si-O or Al-O tetrahedral in the 630-560 cm^{-1} region (Bernes et al., 1999) at 621.08 cm^{-1}, asymmetric Si-O-Si or Si-O-Al tetrahedral vibrations in 1200-800 cm^{-1} region (Wang et al., 2019) at 995.27 cm^{-1}, carbonate C-O vibrations in 1470-1410 cm^{-1} region (Zhao et al., 2022) at 1417.68; 1446.41; and 1483.36 cm^{-1}, asymmetric O-H bending vibration in the 3200-3000 cm^{-1} region (Zhuang et al., 2020) at 3161.33 cm^{-1}, Si-OH or Al-OH bending vibrations in the 3440 cm^{-1} region at 3469.94 and 3522.02 cm^{-1}.

The red mud B shows several absorption peaks, including the Fe-O stretching vibration group in the 500-400 cm^{-1} region (Bernes et al., 1999) at 439.77 cm^{-1}, cyclic vibration of Si-O or Al-O tetrahedral in 630-560 cm^{-1} region (Bernes et al., 1999) at 623.01 cm^{-1}, asymmetric Si-O-Si or Si-O-Al tetrahedral vibrations in 1200-800 cm^{-1} region (Wang et al., 2019) at 995.27 cm^{-1}, carbonate C-O vibration in 1470-1410 cm^{-1} region (Zhao et al., 2022) at 1417.68; 1450.47 cm^{-1}, CO_3^{2-} stretching vibration at 804.32 cm^{-1}. The presence of carbonate and CO_3^{2-} C-O bond functional groups confirmed the presence of Na_2CO_3 (Shang et al., 2003; Chandran et al., 2007). In addition, there is also asymmetric O-H bending vibration in the 3200-3000 cm^{-1} region (Zhuang et al., 2020) at 3161.42 cm^{-1}, Si-OH or Al-OH bending vibration in the 3440 cm^{-1} regions at 3462.22 and 3523.95 cm^{-1}.

The results of the interpretation of red mud A and B show that the increase in heating temperature on red mud does not affect the shift in the peak of functional groups. However, based on the research of Liu et al. (2013), the calcination temperature of 200°C is the best calcination temperature of red mud as a catalyst in methyl ester synthesis with the maximum methyl ester product yield. In addition, increasing the temperature of red mud from 100°C to 200°C also decreases its solubility in methanol, which will reduce the occurrence of leaching on the catalyst.

3.2 Transesterification from good quality BCPO (FFA = 0.36%) using red mud catalyst

The transesterification reaction was carried out by reacting methanol with red mud catalyst first in a three-neck flask for 10 minutes at 65°C, followed by adding BCPO. The mixture of methanol with a catalyst formed methoxy compounds (CH_3O^-). Methoxy ions in the transesterification reaction were nucleophilic from the reaction between the catalyst's active site and methanol. The methoxy ion attack the carbonyl group on the triglyceride, leading to tetrahedral intermediates forming methyl esters and diglyceride anions. The diglyceride anion also reacted with methanol to produce a methoxy ion. The methoxy ion then attacks the carbonyl group on the diglyceride to produce monoglyceride and methyl ester. The methoxy ion attacks the carbonyl carbon atom of monoglyceride to produce methyl ester and glycerin (Hambali et al., 2008; Kusuma et al., 2013).

Determination of the mole ratio of BCPO: methanol aims to determine the volume of methanol that can produce maximum conversion of methyl ester products. The synthesis was carried out using a 5% catalyst with variations in BCPO:methanol mole ratio, including 1:10, 1:15, and 1:20, and 3 hours of reaction until the following results were obtained.

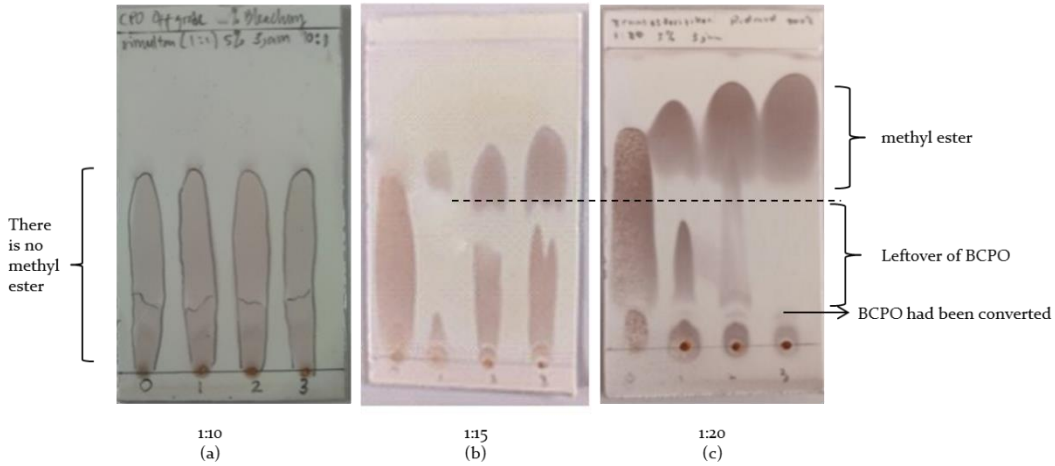

Figure 3. TLC result each hour (0, 1, 2, and 3) synthesis of methyl ester by transesterification with mole ratio variation 1:10 (a); 1:15 (b); 1:20(c)

Table 1. Interpretation of methyl ester stain of transesterification synthesis results on the TLC plate

BCPO:methanol (n/n)	Time (h)		
	1	2	3
1:10	-	-	-
1:15	*	*	*
1:20	*	*	**

description: - (not formed) * (partially conversion)
** (total conversion)

Liu et al. (2013) have conducted research on the synthesis of methyl esters from soybean oil using a red mud catalyst with a mole ratio of BCPO:methanol (1:24), 4% catalyst, temperature 65°C with a calcination temperature variation of 200°C to obtain a methyl ester conversion % of 94%. Meanwhile, it can be observed that the red mud B catalyst used in this study produced total methyl ester conversion at a BCPO:methanol mole ratio of 1:20 for 3 hours. This mole ratio is the optimum BCPO:methanol mole ratio in synthesizing methyl ester by transesterification.

3.3 Esterification from low quality BCPO by esterification using Sn-zeolite catalyst.

The esterification reaction in this study using raw materials that have a FFA content of 20.863% using Sn-zeolite catalyst was carried out at a concentration of 5%, time 3 hours with a mole ratio of BCPO: methanol 1:10, 1:15, and 1:20. The fatty acid esterification reaction with Sn-zeolite was catalyzed by

Bronsted acid sites. The acid sites can enhance the protonation of fatty acid carbonyl groups. Protonation results in increasing the positive charge of the carbon atom of the fatty acid carbonyl group so that it becomes a good target for nucleophiles (oxygen atoms in methanol). At this stage, a C-O bond will be formed. Then, one of the hydroxyl groups is protonated involving the breaking of the C-O bond and the release of water. The protonated ester releases its proton. The result of this process is the substitution of the OH group into OR' (Hart et al., 2003).

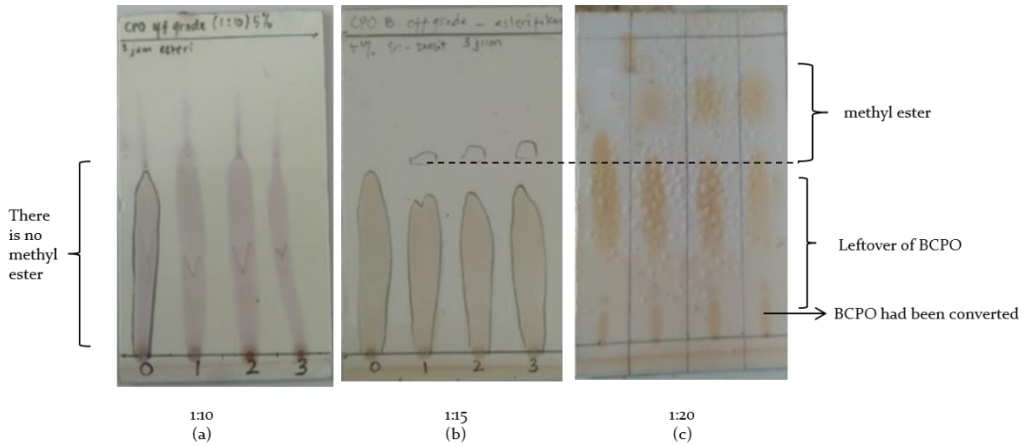

Figure 4. TLC result in each hour (0, 1, 2, and 3) synthesis of methyl ester by esterification with mole ration variation 1:10(a); 1:15(b); 1:20(c)

Table 2. Interpretation of methyl ester stain of esterification synthesis results on the TLC plate

BCPO:methanol (n/n)	Time (h)		
	1	2	3
1:10	-	-	-
1:15	*	*	*
1:20	*	*	*

description: - (not formed) * (partially conversion)
** (total conversion)

3.4 Simultaneous (Transesterification-Esterification) Synthesis of Methyl Ester from BCPO Using Sn-Zeolite And Red Mud Catalysts

In this study, the simultaneous transesterification-esterification reaction was carried out by using raw materials with an FFA content of 20.86% using Sn-zeolite and red mud catalysts. The Sn-zeolite catalyst was synthesized from zeolite impregnated with Sn. Alcoholic reactions are generally applied to synthesizing methyl esters where the breakdown of a functional group/compound uses reactants in the form of reactive alcohol compounds with specific compositions and conditions/treatments and a particular time. Optimum conditions such as the ratio of Sn-zeolite and red mud catalysts, catalyst concentration (%), and BCPO:methanol mole ratio were investigated.

The parameter can be seen by determining the methyl ester stain on a thin layer chromatography (TLC) plate. The hourly TLC test results of the synthesis showed that methyl esters were not identified. However, after separating the catalyst using centrifugation, separation with a separating funnel, and TLC again obtained at the top of the separation, there was a methyl ester stain.

Determination of the best mass ratio Sn-zeolite:red mud

Figure 3 shows that the best mass ratio of catalysts in the esterification reaction of low-quality BCPO is Sn-zeolite: red mud = 1.5: 1. Sn-zeolite catalyst can reduce FFA to 11.92%, where the decrease in FFA illustrates the conversion of methyl esters by esterification. The esterification reaction using an Sn-zeolite catalyst occurred within the distributed pores and matches the molecular size of the reactants. The catalyst's hydrophobic nature also facilitates reactant adsorption into the pore mouth. The reactants

undergo internal diffusion from the pore mouth through the zeolite pores. The reactants was adsorbed onto the active surface of the catalyst so that the esterification reaction take place. At the end of this reaction, methyl esters and other products will be desorbed from the active surface and diffused to the outer surface of the catalyst (Fogler, 2006).

Figure 3. Final FFA value after methyl ester synthesis at variation of catalyst mass ratio

Determination of the best concentration of catalyst (%)

The best catalyst concentration in the esterification reaction of low-quality BCPO can reduce FFA to 9.75%. The catalyst concentration influences the increase in product conversion only to a certain extent. When the concentration was increased, there was no a significant effect because the catalyst has the proper action to convert fatty acids into esters (Kurniasih, 2012). According to Padmaningsih et al. (2006), methanol can act as a reactant and a protic solvent that can balance the anions formed from the catalyst after releasing protons (from Bronsted acid sites). As a result, an excess catalyst causes more methanol to function as a catalyst solvent than as a reactant, thus reducing product conversion.

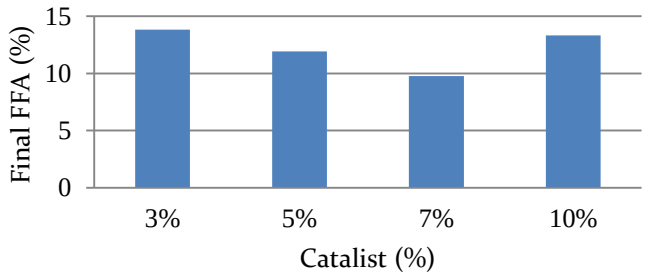

Figure 4. Final FFA value after methyl ester synthesis at variation of %catalyst

Methanol can act as a reactant and a protic solvent that balances the anions formed from catalysts that have released protons (from Bronsted acid sites). As a result, excess catalyst results in more methanol functioning as a catalyst solvent than as a reactant, thus reducing product conversion (Prakoso et al., 2007).

Determination of the best mole ratio of BCPO: methanol

The best catalyst concentration in the esterification reaction of low-quality BCPO reduced FFA to 8.31%. The esterification reaction of fatty acids and methanol follows the concept of Le Chatalier equilibrium, where the methyl ester formation reaction goes both ways (back and forth). One concept of shifting the equilibrium is adding reactants and shifting the equilibrium towards the product (Chang, 2005). Thus, the molar ratio of fatty acids and methanol is one of the factors that can affect the conversion and quality of methyl esters. Conversion occurred when the molar ratio of BCPO:methanol was increased to 1:20.

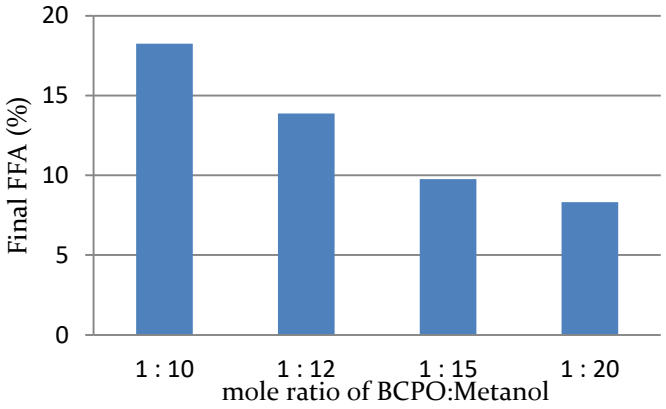

Figure 5. Final FFA value after methyl ester synthesis at variation ratio mole BCPO:methanol

After synthesis, the product was separated from the catalyst using centrifugation. The results of simultaneous methyl ester synthesis using acid and base catalysts will produce several components such as methyl esters, residual oil, residual methanol, water, and glycerol so that further separation and purification are needed to obtain pure methyl esters. Liquid-liquid separation was carried out using a separating funnel based on solubility in certain solvents with different phases (Febrianti et al., 2019). The top is a mixture of residual BCPO, residual methanol, and methyl ester, while the bottom is glycerol.

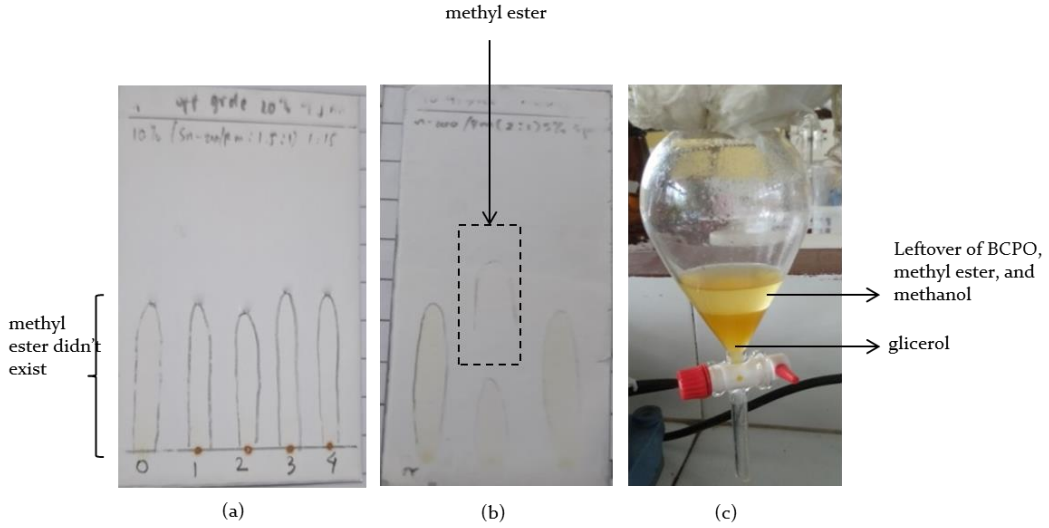

Figure 6. (a) TLCs result each hour synthesis; (b) TLC result after separating product; (c) Extraction result by separating funnel.

Based on the explanation above, the best condition for the synthesis of methyl esters from BCPO was obtained by a decrease in the % of free fatty acids in BCPO from 20.86% to 8% at the synthesis condition of 7% catalyst, acid:base ratio (1.5:1) and a mole ratio of BCPO:methanol 1:20 with no total conversion product as can be seen in **Figure 6**. The low percentage of products produced can be influenced by factors such as high FFA content. Rattanaphra et al. (2010) explained that with the increasing amount of FFA in the simultaneous transesterification-esterification reaction, the transesterification reaction rate would decrease while the rate of fatty acid methyl ester formation through the esterification reaction increases. The rapid formation of esters can cause this.

In addition, the accumulation of methyl esters and water in the mixture promotes the reverse reaction to form free fatty acids from triglyceride hydrolysis. The catalyst pore acts as a microreactor that makes it possible to obtain the desired catalytic reaction according to selectivity (Handoko, 2003). As mentioned above, sodium in red mud is present freely and bound in the form of $NaCO_3$. Using acidic

catalysts can lead to the formation of water in the mixture and ultimately lead to the termination of the reaction before the reaction is complete (Saefudin, 2005).

4. Conclusion

The best condition for the synthesis of methyl ester by transesterification is at 5% catalyst, 3 hours reaction time, and the best BCPO:methanol mole ratio of 1:20 with total conversion. The best condition for the synthesis of methyl ester by esterification is at 5%; 3 hours reaction time; and the best BCPO:methanol mole ratio of 1:20 with non-total conversion. The best condition for the simultaneous synthesis of methyl ester is at the ratio of Sn-zeolite:red mud = 1.5:1, time 3 hours, 7% catalyst, and BCPO:methanol mole ratio of 1:20 with non-total conversion.

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