



The Effect of Tetrahydrofuran on Transesterification of Palm Oil Using Modified Clay Catalyst into Biodiesel

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Abstract : Transesterification of palm oil into biodiesel has been done using modified clay catalyst. The modified clay catalyst was synthesized by destructing the clay with 8M HCl solution, then fusion by NaOH pellet (NaOH/clay ratio = 0.8), followed by treating with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, CTAB and distilled water. Then the mixture was regulated to pH of 11.5. Next, the mixture was then poured into a reactor for hydrothermal process at 140 °C for 48 h. The results of the dealumination of clay was characterized by X-ray Fluorescence and the synthesized zeolite was characterized using surface area analyzer and X-Ray Diffraction. The transesterification of palm oil (PO) process was carried out in the variation of temperatures of 55 and 65 °C. Ratio of catalyst : PO : methanol was 1.0 : 20.0 : 13.3 and reaction time was 6h. The liquid product was analyzed using Gas Chromatography Mass Spectrometer. The result showed that the dealumination of clay had Si content of 34.77 % and Al of 5.67 %. The modified clay (MC) had surface area of 5.5685 m²/g, pore volume of 0.0126 cm³/g, and pore diameter of 8.871 nm. The results of measurements with XRD produced a different form of chromatogram and type of mineral. The main mineral was gismondine. In this research, the transesterification reaction of PO at a temperature of 55 °C using MC catalyst without THF resulted methyl esters (biodiesel) of 41.5 wt%. Furthermore, after adding THF with ratio of methanol : THF of 1 : 1 and the same treatment, the resulting methyl ester (biodiesel) was the same phase (a one-phase) and methyl esters (biodiesel) product was more than 100 wt%..

Keywords : clay, modified, transesterification, one-phase, biodiesel.

Introduction

Biodiesel is an alternative energy that can be used as fuel like fossil fuel. Biodiesel is obtained from vegetable oil or animal oil so it can be renewed. Since biodiesel is a non-fossil oil it is certainly free from sulfur, which will have a positive impact on the environment. Biodiesel has advantages compared to petroleum diesel fuel derived from petroleum, among others, has a better lubrication properties that can extend engine life,

is a safe fuel, easy to handle, and non-toxic, has a relatively low exhaust gas. The production of sustainable alternative fuels is attracting increasing academic and industrial interest. Biodiesel, a non-petroleum-based, is one of these sustainable fuels and it has many advantages such as low emissions, biodegradability and better lubricity¹. Biodiesel can be made through an esterification or transesterification reaction. Esterification is normally carried out in a homogeneous phase in the presence of acid catalysts such as H₂SO₄, HF, H₃PO₄, HCl²⁻³. In the esterification reaction will produce biodiesel and water⁴. Transesterification reaction can be done in a homogeneous phase in the presence of base catalyst such as NaOH, KOH. Moreover, and these catalysts in homogeneous catalysts are hazardous and corrosive liquid acids. So this catalyst needs to be reviewed in its use. In recent years, the development of alternative fuel like bioethanol and biodiesel from renewable sources has received considerable attention. Homogeneous catalysts are used but they have problems such as leaching, saponification which require washing and this cause release of waste water. Therefore, heterogeneous catalysts can be considered as an alternative to minimize environmental damage and reduce biodiesel cost. There has been tremendous upsurge of interest in the use of different heterogeneous and environment friendly catalysts for various organic transformations. In recent years, such catalysts can help to minimise waste production, render the synthetic process more attractive from both the environment and process economic point of view. The solid catalysts can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form. As they can be recycled, the process becomes less expensive and at the same time the contamination of the products by trace amount of metals is avoided. Heterogeneous solid catalysts such as zeolites and clay minerals have been developed as substitutes for homogeneous catalysts and have benefit of being easy to recover and the process required no washing⁵. One of heterogeneous catalyst is zeolite⁶⁻⁹. Zeolite have been widely used as industrial heterogeneous catalyst because they are inexpensive and environmentally benign. They offer generous surface area and high porosity¹⁰. The advantage of using heterogeneous catalyst like zeolite is that it can be used repeatedly and easier to separate than the homogeneous catalyst treatment. It is interesting why heterogeneous catalyst in the synthesis of biodiesel should be considered.

Zeolite is porous solid composed of silica and alumina framework that can be used as support. Thus, the basic ingredients for zeolite synthesis are SiO₂ and Al₂O₃ which can be obtained from clay, for example from Merauke clay in Merauke District Papua Province, Indonesia. The clays form hard lumps when dry and sticky when wet. This property is determined by the type of clay minerals that dominate it. Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations found on or near some planetary surfaces. From this explanation, the clay will not be effective if it is used as a catalyst without being modified until the content that does not function as a catalyst will come out.

Clay also has silica content (SiO₂) and alumina (Al₂O₃) that is still fused and chemically bonded in it. The treatment of the clay include destruction using HCl at high concentration and fusion with NaOH pellet to obtain free of silica and alumina as the raw material for the synthesis of zeolite¹¹⁻¹³. Silica and alumina free obtained from fusion of clay can be used for synthesis of zeolite. Zeolite synthesis using hydrothermal methods has been carried out and it is reported that the formation reaction can occur at temperatures around 25-150 °C.¹⁴

The use of co-solvent becomes an appropriate alternative to solve the problem of solubility. A one-phase reaction can be formed by adding a solvent that can increase the solubility of the oil, the solvent here in after referred to as co-solvent¹⁵. Co-solvent is very soluble with alcohol, fatty acids and triglycerides. The used co-solvent should not contain water and the more co-solvent added is better because it will increase the solubility of the oil. The selected co-solvent has a boiling point close to methanol which can facilitate the separation process at the end of the reaction. Several co-solvents has been used for transesterification reaction including n-hexane, diethyl ether, acetone, 2-propanol, tetrahydrofuran, or ethyl acetate.

Experimental

Materials

Clay was obtained from Merauke, Papua Province, Indonesia. The chemicals used were HCl 37%, NaOH pellet, AlCl₃.6H₂O, Tetrahydrofuran, pH universal paper that purchased from E. Merck, and cetyltrimethylammonium bromide (Aldrich). Aquadest was purchased from Chemistry Lab, Department of Chemistry Faculty of Science and Mathematics, Cenderawasih University, Jayapura, Indonesia. Palm oil used 1 which was purchased from a traditional market in Jayapura.

Instrumentation

X-Ray Fluorescence spectrometry (XRF): Bruker S2 Ranger , Surface area analyzer : NOVA 1200 (QUANTACHROME), X-Ray Diffraction (XRD): Shimadzu-6000 XRD, Gas Chromatography - Mass Spectrometer (GC-MS): GS-2010 Shimadzu.

Procedure

Modified Clay into Mineral with Si/Al Ratio of ± 5

After being washed and separated with water then the clay dried in oven at temperature of 120 °C for 4 h. The clay was grinded and sieved (100 mesh). Next, the clay (50 g) was destructed using 100 mL of 8M HCl followed by refluxing the mixture for 6 hat temperature of 100°C. The clay was filtered and washed using deionized aquadest until neutral condition, dried on the oven at 120 °C for 4 h. Furthermore, the clay results of dealumination was fused with NaOH pellet (NaOH/zeolite ratio = 0.8), then calcined at 500°C for 4 h. Subsequently synthesis was carried out as follows:

The clay results of fusion (10 g) was mixed with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1.2 g) , CTAB (1.2 g) and distilled water was added to adjusted pH 11.5 while stirring for 48 h at room temperature.

Then the sample was done hydrothermally treated at 140°C for 48 h. The synthesized zeolite or modification of clay (MC) was then washed using aquadest until the solution reached pH of 6, then filtered followed by dried on the oven at 120 °C for 4 h and calcined at 350°C for 3 h.

Transesterification Process

Before transesterification process, the first, palm oil (PO) was absorbed with modified clay without fusion treatment. Then, transesterification reactions was carried out in 250 mL double-neck flask connected to reflux condenser and equipped with thermometer. First, put methanol (20 g) and catalyst from results of synthesis (1.5 g) mixed and then heated to temperature of 50°C while stirring using a magnetic stirrer, after reaching this temperature, then put PO (30 g), Next the temperature raised to 65°C while stirring for 6 h

After completion of the reaction, the mixture was cooled then separated between solid fraction (catalyst) and the liquid fraction in the form of methyl ester and glycerol. The mixture of methyl ester and glycerol were put in separating funnel and left for 30 h. Then the methyl ester was separated and weighed.

Transesterification process was also carried out with reaction treatment of :

- 65°C using /MC catalyst and added THF with methanol : THF ratio of 2 : 1.
- 55 °C using MC catalyst and added THF with methanol : THF ratio of 1 : 1.
- 55 °C using /MC catalyst and added THF with methanol : THF ratio of 1 : 2.

Methyl ester was analyzed using GC-MS. The conversion was calculated by following formula:

$$\text{Liquid product as methyl ester conversion [wt \%]} = \frac{W_2 \text{ (g)}}{W_1 \text{ (g)}} \times 100\%$$

where, W_1 = initial feed weight (before transesterification process)

W_2 = methyl ester product weight (g)

Result and Discussion

Results of Measurement Si and Al of dealumination of Clay Using X-Ray Fluorescence spectrometry (XRF)

For modification of clay into zeolite with Si/Al ratio = ± 5 , it is necessary to know Si and Al content in clay after dealumination. Clay is heterogeneous system which consists of silica systems and alumina silica systems as well as other impurities such as organic materials. Clay minerals are hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations found on or near some planetary surfaces. The silica system and organic impurities are parts that are not

active as catalysts or can also be referred to as catalyst impurities, so the contents that can inhibit the catalytic process need to be removed. Interaction with 8M HCl solution can also react with metals contained in clay so that it causes the occurrence of dealumination and decationation, namely the release of Al and other cations such as Fe^{2+} , Mn^{+} in the contents of clay. However, interaction with 8M HCl, in certain clay does not cause the clay to be decomposed into silica and alumina free which is the raw materials of zeolite synthesis. The results of measurements with XRF after dealumination of clay with 8M HCl was obtained Si of 34.77% and Al of 5.67%. From this result, it is necessary by adding Al to form Si/Al with ratio of ± 5 . which can be derived from $AlCl_3 \cdot 6H_2O$.

Results of Analyze of MC Catalyst Using Surface area analyzer and X-Ray Diffraction

The surface area, pore volume and pore diameter were $5.558 \text{ m}^2/\text{g}$, pore volume of $0.0129 \text{ cm}^3/\text{g}$, and pore diameter of 9.352 nm respectively. The pore diameter of 9.352 nm was mesopore in synthesis of zeolite. The XRD results for clay before modification is in Figure 1 as follows:

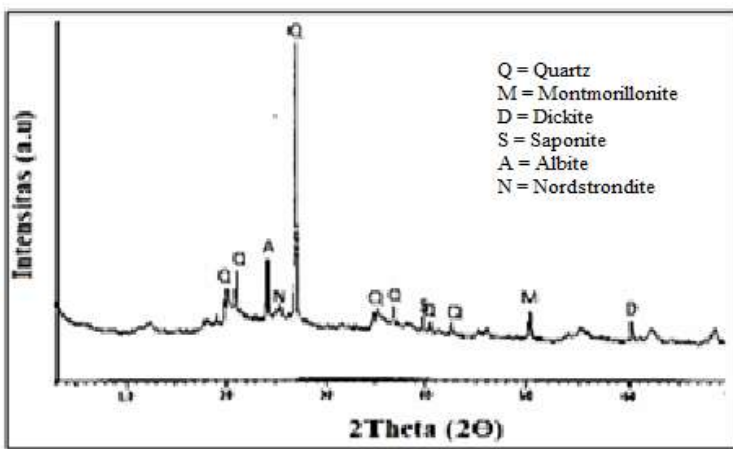


Figure1. Diffractogram of Merauke clay before modification

Base on MPDF (Mineral Powder Diffraction File), From the data above, it was then used to identify the difactogram peaks in Figure 1. It could be identified that the types of minerals were Quartz (SiO_2); Albite ($NaAlSi_3O_8$); Nordstrandite ($Al(OH)_3$); Saponite [$Ca_{0.25} (Mg,Fe)_3 (Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$]; Dickite [$Al_2Si_2(OH)_2$]; Montmorillonite [$(Al_{1.67}Mg_{0.33})Si_4O_{10} (OH)_2Na_{0.33}$] respectively. Quartz mineral was dominant in the clay of Merauke. Next to the modification of clay (MC), base on JCPDS (Joint Committee on Powder Diffraction Standards), the XRD results in Figure 2.

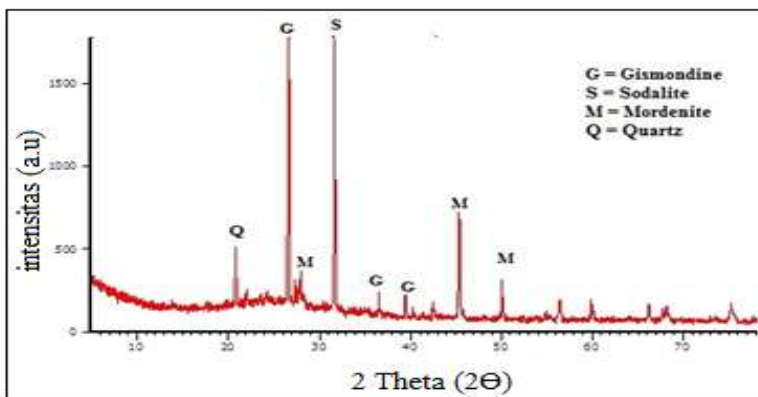


Figure 2. Diffractogram of MC catalyst

Based on 2θ of the results XRD diffractogram of the MC presented in Figure 2 showed that result of modified clay composed of crystalline peaks were sharper and higher than the Clay before modification (Figure 1). The highest peak at $2\theta = 26.65$, $d = 3.34$. Base on 2θ the results of the diffractogram were 20.87 ,

d = 4.26 (Quartz) ; 26.65, d = 3.34 (Gismondine) ; 27.38 , d = 3.25 (Mordenite) ; 27.96 , d = 3.19 (Mordenite) ; 31.69, d = 2.82 (Sodalite) ; 45.41 d = 1.99 (Mordenite) ; 45.56 , d = 1.99 (Mordenite) ; 50.14 , d = 1.81 (Mordenite) respectively. Gismondine zeolite was the dominant mineral of the MC. Synthesis of zeolite from raw material that its silica and alumina were still fused and chemically bonded such as clay, natural zeolite, fly ash, volcanic ash generally produced a mixture zeolite¹⁶⁻¹⁹.

Result of transesterification reaction using MCcatalyst

Onthe transesterification process, the MC catalyst and methanol were mixed before reacted with PO. The aim is to form sodium methoxide. The reaction can be written as follows:



MC catalyst had Na content so that in this reaction NaOCH₃ obtained and it is a Lewis base site, because it has a free electron pair. This methoxide ion is an active intermediate compound in the transesterification reaction. When the Palm oil was inserted into the reactor, NaOCH₃ will interact with triglycerides, so the fatty acids contained in the triglycerides will break down to form fatty acid methyl esters (FAME) through the mechanism of SN₂ mechanism. In general, the transesterification reaction can take place using heterogeneous catalysts, for example modified clay can be written as follows:

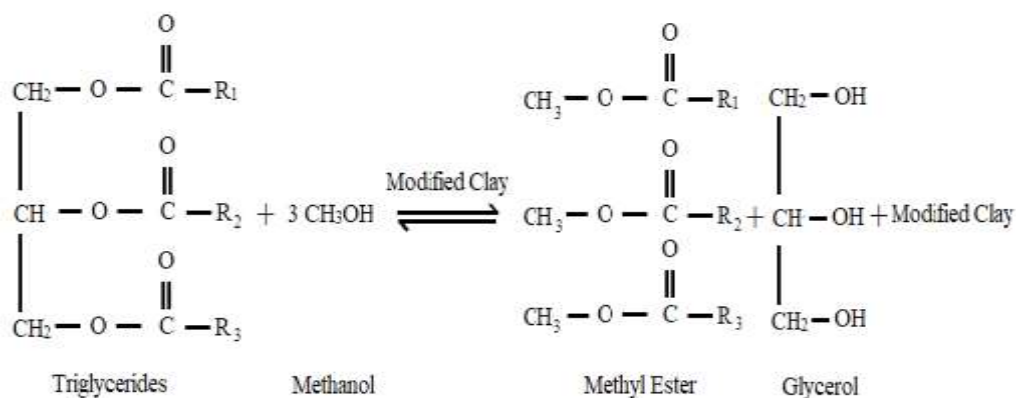


Figure 3. Transesterification reaction using heterogeneous catalyst

The results of the above transesterification reaction is in the form of a mixture. The contents of the mixture are methyl esters at the top, glycerol and catalyst at the bottom. Next, the methyl ester and glycerol were separated. Catalyst could easily be separated again because it was solid. Investigation of the effect of temperature and tetrahydrofuran on the transesterification of palm oil using a MC catalyst has been carried out. Temperature has an effect on increasing the reaction rate. If the temperature in a reaction is raised, it will cause the reactant particles to move more actively, so that collisions between reactant molecules are increasingly common, and have an impact on the faster the product is formed. The presence of a catalyst causes the product to form faster than the without catalyst. Thus the faster the biodiesel fraction also occurs

The following Figure 4 was results of transesterification of PO using MC catalyst without tetrahydrofuran and with THF at temperature of 55 and 65 °C.

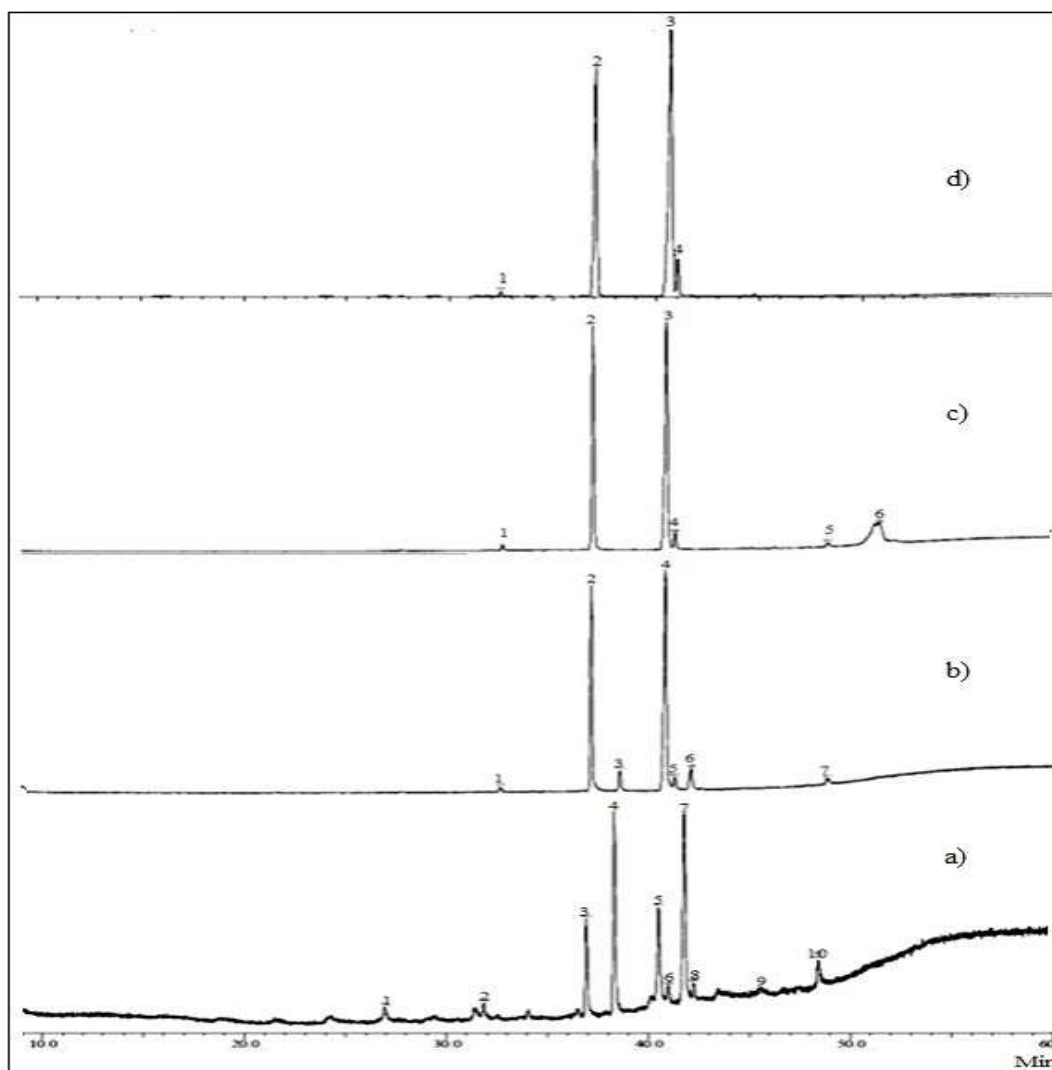


Figure 4. GC-MS chromatogram of transesterification product of PO using MC catalyst

- a) Temperature of 65°C without THF;
- b) Temperature of 65°C with THF (ratio of methanol:THF of 2 : 1)
- c) Temperature of 55°C with THF THF (ratio of methanol:THF of 1:2)
- d) Temperature of 55°C with THF THF (ratio of methanol:THF of 1:1)

From Figure 4, there were differences in the results of the transesterification reaction between the catalyst and added THF as well as temperature of reaction. This difference can be seen from the chromatogram peaks produced. From these peaks could be stated the amount of methyl esters produced. Then it can be explained as follows:

In Figure 4a, based on the chromatogram, there were 10 retention time detected with chemical constituents that were different. The retention time with the resulting compound found in Table 1.

Table 1. Yield of transesterification of Palm oil using MC catalyst without THF at 65 °C

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	26.951	Undecane, 4- methyl	1.10
2	31.845	Tetradecane	1.17
3	36.934	Hexadecanoic acid, methyl ester	13.41
4	38.319	Hexadecanoic acid, methyl ester	28.01
5	40.511	9-Octadecanoic acid, methyl ester	15.47
6	40.979	Octadecanoic acid, methyl ester	1.51
7	41.783	9-Hexadecenoic acid	32.92
8	42.230	Hexadecanoic acid, ethyl ester	2.51
9	45.092	Heptanoic acid, 3,6,6-trimethyl-, methyl ester	0.57
10	48.257	Di-n-octyl phthalate	3.32

From Table 1, there were 5 methyl esters (no 3, 4, 5, 6 and 9), the others were not methyl esters. The dominant methyl esters (FAME) were 9-Hexadecenoic acid, methyl ester ($C_{16}H_{30}O_2$) that content of 32.92 %; Hexadecanoic acid, methyl ($C_{17}H_{34}O_2$) that content of 28.01 %; and 9-Octadecenoic acid methyl ester ($C_{19}H_{36}O_2$) that content of 15.47 % respectively.

Furthermore, in Figure 4b, there were many fatty acids with peak number fewer. Based on the chromatogram, there were 7 retention time detected with chemical constituents that were different. The retention time with the resulting compound found in Table 2.

Table 2. Yield of transesterification of Palm oil using MC catalyst + THF at 65 °C (ratio of methanol : THF = 2 : 1)

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	32.567	Tetradecanoic acid, methyl ester	0.79
2	37.009	Hexadecanoic acid, methyl ester	35.20
3	38.384	Hexadecanoic acid, ethyl ester	3.53
4	40.620	9-Octadecenoic acid, methyl ester	51.34
5	41.075	Octadecanoic acid, methyl ester	2.98
6	41.874	Hexadecenoic acid	4.49
7	48.544	Benzenedicarboxylic acid, dioctyl ester	1.19

From Table 2, there were 5 methyl esters (no 1, 2, 3, 4 and 5), the others were not methyl esters. The dominant methyl esters (FAME) were 9-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$) that content of 51.34 %; Hexadecanoic acid methyl ester ($C_{17}H_{34}O_2$) that content of 38.73 %; and Octadecanoic acid, methyl ester ($C_{19}H_{38}O_2$) that content of 2.98 % respectively.

In Figure 4c, based on the chromatogram, there were 6 retention time detected with chemical constituents that were different. The retention time with the resulting compound found in Table 3.

Table 3. Yield of transesterification of Palm oil using MC catalyst + THF at 55 °C (ratio of methanol : THF = 1 : 2)

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	32.716	Tetradecanoic acid, methyl ester	0.82
2	37.124	Hexadecanoic acid, methyl ester	35.11
3	40.702	9-Octadecenoic acid, methyl ester	46.37
4	41.111	Octadecanoic acid, methyl ester	2.73
5	48.537	1,2-Benzenedicarboxylic acid, dioctyl ester	0.65
6	51.018	Dodecanoic acid, ethenyl ester	14.32

Next, in Figure 4d, based on the chromatogram, there were 4 retention time detected with chemical constituents that were different. The retention time with the resulting compound found in Table 4.

Table 4. Yield of transesterification of Palm oil using MC catalyst + THF at 55 °C (ratio of methanol : THF = 1 : 1)

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	32.473	Tetradecanoic acid, methyl ester	0.54
2	37.102	Hexadecanoic acid, methyl ester	37.94
3	40.746	9-Octadecenoic acid, methyl ester	56.46
4	41.065	Octadecanoic acid, methyl ester	4.89

From Table 4, All of retention time that detected were methyl esters. The dominant methyl esters (FAME) were 9-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$) that content of 56.46 %; Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$) that content of 37.94 %; and Octadecenoic acid, methyl ester ($C_{19}H_{34}O_2$) that content of 4.89 % respectively.

From Figure 4b, c and d, and pay attention to Tables 2, 3, and 4, each catalyst produced by the dominant fraction was almost the same. The transesterification reaction of PO using MC catalyst without THF at a temperature of 65°C resulted methyl esters (biodiesel) of 83 wt %. Furthermore, after adding THF to the same treatment, the resulting methyl ester (biodiesel) was 93.7 wt%. This indicates that THF can increase the yield of methyl esters. However, the temperature of transesterification must consider the type of alcohol used. The transesterification reaction of PO at a temperature of 55 °C using MC catalyst resulted methyl esters (biodiesel) of 41.5 wt %. The catalytic reaction of transesterification at 55 °C does not run optimally because the temperature has not yet approached the boiling point of methanol. While at temperatures has passed the boiling point of methanol, the transesterification also does not run optimally.²⁰⁻²² Furthermore, after adding THF with ratio of methanol : THF of 1 : 2 and the same treatment, the resulting methyl ester (biodiesel) was 63.7 wt%. Next, after adding THF with ratio of methanol : THF of 1 : 1 and the same treatment, the resulting methyl ester was the same phase (a one-phase) and methyl esters (biodiesel) product was more than 100 wt %. Although it did not be done at a temperature of 65 °C. At temperature of 65 °C is the temperature around the boiling point of methanol which is 64.7 °C. The optimal temperature is 64.7 °C (near the evaporation temperature of methanol)²³. However, the addition of THF maximum results do not have to be at a temperature of 65 °C. THF (Tetrahydrofuran) function is as a co-solvent. Co-solvent is very soluble with alcohol, fatty acids and triglycerides. The used co-solvent should not contain water and the more co-solvent added is better because it will increase the solubility of the oil. The use of co-solvent becomes an appropriate alternative to solve the

problem of solubility. A one-phase reaction can be formed by adding a solvent that can increase the solubility of the oil, the solvent here in after referred to as co-solvent¹⁵.

Conclusion

Modification of Merauke clay with Si/Al Ratio of ± 5 through dealumination followed by fusion with NaOH pellets then hydrothermal reaction for 48 h at temperature of 140 °C produced some types of zeolite minerals. The dominant mineral was gismondine zeolite. The modified form of clay was used as catalyst (MC catalyst) for the transesterification of Palm oil into biodiesel.

In this study, the transesterification of Palm oil using MC catalyst with adding tetrahydrofuran could increase the amount of yield of methyl esters (FAME) compared to modified clay (MC) catalysts without tetrahydrofuran at the same temperature. The transesterification reaction of Palm oil at a temperature of 55 °C using MC catalyst and adding THF with ratio of methanol: THF of 1 : 1, the resulting methyl ester was the same phase and methyl esters (biodiesel) product was more than 100 wt %. Although it did not be done at a temperature of 65 °C. The dominant methyl esters (FAME) were 9-Octadecenoic acid, methyl ester (C₁₉H₃₆O₂) that content of 56.46 %; Hexadecanoic acid, methyl ester (C₁₇H₃₄O₂) that content of 37.94 %; and Octadecenoic acid, methyl ester (C₁₉H₃₄O₂) that content of 4.89 % respectively.

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