Biodiesel Synthesis Through Transesterification of Used Cooking Oil Using NaN₃/Modified Clay Catalyst and The effect of Acetone as Co-Solvent

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Abstract : Transesterification of used cooking oil (UCO) using NaN_3/modified clay catalyst and investigation of the acetone effect have been done.The modified clay catalyst was synthesized by destructing the Merauke clay with8M HCl solution, then fusion by NaOH pellet, followed by treating with $AlCl_3.6H_2O$, 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 byX-ray Fluorescence and the synthesized zeolite was characterized using surface area analyzer and X-Ray Diffraction.The synthesized zeolite was impregnated by NaN_3 as a precussor produced the NaN_3/modified clay catalyst sample.Rasio of catalyst :UCO : methanol was 1.0 : 20.0 : 13.3 and the ratio of aceton to methanol was 2:1. The transesterificationprocess was carried out at 60 and 65°C. The liquid product   was analyzed using Gas Chromatography Mass Spectrometer.The resulted showed that themodified clay had surface area of 5.5685 m^2/g, pore volume of 0.0126 cm^3/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 of UCO using NaN_3/MC catalyst at 60 °C resulted methyl esters of 65.3 wt %.Furthermore, after adding acetone to the same treatment, the resulting methyl ester was 82.7 wt%.The transesterification of UCO at 65 ° C using NaN_3/MC catalyst and acetone produced the highest content of methyl esters or biodiesel that was equal to 94.4 wt %.

Keywords : clay, modified, transesterification, acetone, biodiesel.

Introduction

Repeated or continuous frying oil will produce free fatty acids and peroxide numbers as well as compounds such as ketones, aldehydes, polymers and increased free radicals so that to some extent the oil is no longer suitable to be used which is called used cooking oil[1]. Even though the results of repeated cooking (used cooking oil)not suitable for using because it is harmful to health, but there are still some people who continue to use it for food preparation purposes. Furthermore, the community throws away used cooking oil as waste (waste cooking oil). Waste cooking oil (WCO) is the result of repeated fryingwhich is generated daily from various sources comprising households, restaurants, catering establishments, and industrial kitchens[2]. This waste, if it is disposed of in the environment, for example in an aquatic area, the water channel will reduce the quality of the area. So an alternative use is needed. One of the alternative use of waste cooking oil is to be converted into biodiesel, because it contains triglycerides.Biodiesel can be made through an esterification or transesterification reaction and requires a catalyst.Catalystis generally definedas material thatcanaccelerate chemical reactioninto product.At the end of the reaction after the product is formed the catalyst will reappear as the same compound as before.

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 lubricity[3]. 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 H_2SO_4, HF, H_3PO_4, HCl[4-5]. In the esterification reactionwill produce biodiesel and water[6]. 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 washing[7].One of heterogeneous catalyst is zeolite[8-11]. Zeolite have been widely used as industrial heterogeneous catalyst because they are inexpensive and environmentally benign. They offer generous surface area and hight porosity[12].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 SiO_2 and Al_2O_3 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 (SiO_2) and alumina (Al_2O_3) 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 zeolite[13-15]. 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 ^{o}C[16].

One of the problems in the transesterification reaction of biodiesel is the non homogeneity of the reactants involved.Methanol is not soluble with triglycerides. Conventionally to increase the solubility of reactants was carried out with temperature 65°C for 2 hours[17] or with using microwave-assisted reactor[18]. The use of high energy in reaction for a long time leads to inefficiency in biodiesel production. 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 hereinafter referred to as co-solvent[19]. 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. Acetone was found to be the best co-solvent intransesterification reaction[20].

Experimental

Materials

Clay was obtained from Merauke, Papua Province, Indonesia. The chemicals usedwere HCl 37%, NaOH pellet,$AlCl_3.6H_2O$, pH universal paper,Aceton, $NaN_3$from E.Merckthat 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. Used cooking oil used come from palm oil which was purchased from a restaurant 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 Cromatography - Mass Spectrometer (GC-MS): GS-2010 Shimadzu.

Procedure

Modification of Clay into Mineral with Si/Al Rasio of ±5

After being washed and separated with water then the clay dried in oven at temperature of 120 ^{o}Cfor 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 temperatur of 100°C. The clay was filtered and washed using deionized aquadest until neutral condition, dried on the oven at 120 ^{o}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 $AlCl_3.6H_2O$ (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 zeoliteor 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 ^{o}C for 4 h and calcined at 350°C for 3 h.

The NaN_3/modified Clay (NaN_3/MC) catalyst was prepared by a wetness impregnation[21].The NaN_3 loading was 5wt% based on the weight of MC. The NaN_3 precursor of 0.5013 g was solved into 15 mL of H_2O, then 10 g of MC sample was added. The mixture was then evaporated and dried in an oven at 120 ^{o}C for 3 h. The catalyst sample was calcined at 500°C for 4 h.

Transesterification Process

Before transesterification process, the first, used cooking oil (UCO) was absorbed with modified clay without fusion treatment. Nex, transesterification reactions was carried out in 250 mL double-neck flask connected to reflux condenser and equipped with thermometer . Then put methanol (20 g) and MC catalyst (1.5 g) mixed and then heated to temperature of 60°C while stirring using a magnetic stirrer, after reaching this

temperature, then put UCO (30 g) while stirring for 6 h. Transesterification process was also carried out with reaction temperature of : a) 60°C using NaN_3/MC catalyst. b) 60 °C using NaN_3/MC catalyst and added acetone with methanol : acetonerasio of 1 : 2 (NaN_3/MCA catalyst). c) 65°C using NaN_3/MC catalyst and added acetone with methanol : acetonerasio of 1 : 2(NaN_3/MCA catalyst). After completion of the reaction, the mixture was cooled thenseparated 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. Methyl esterwas analyzed using GC-MS. The conversion was calculated by following formula:

$$\text{Liquid product as methyl ester conversion [wt \%]} = \frac{W2\ (g)}{W1\ (g)} \times 100\%$$

where, W1 = initial feed weight (before transesterification process)

W2 = 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 HCl obtained Si of 34.77% and Al of 5.67%.From this result, it is necessary to add Al which can be derived from $AlCl_3.6H_2O$.

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

Result of surface area, pore volume and pore diameter in modified or synthezedresult of clay mineral obtained from nitrogen adsorption.The surface area, pore volume and pore diameter were 5.5685 m^2/g, pore volume of 0.0126 cm^3/g, and pore diameter of 8.871 nm rspectively. The pore diameter of 8.871 nm was mesopore in synthesis of zeolite. The XRD results for clay before modification is in Figure 1 as follows:
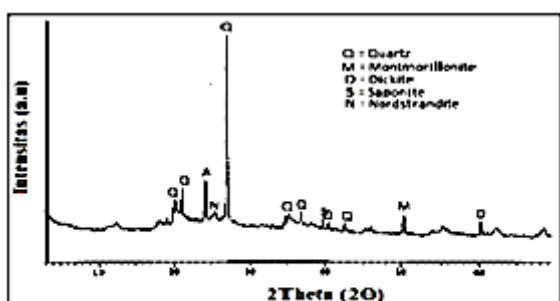
Figure 1. Diffractogram of Merauke clay
before modification

Figure1. Diffractogram of Meraukeclay before modification

Base on MPDF (Mineral Powder Diffraction File), From the data in Figure 1, it was then used to identify the difactogram peaks in Figure 1. It could be identified that the types of minerals werequartz (SiO_2);

albite $(NaAlSi_3O_8)$; nordstrandite $(Al(OH)_3]$; saponite$[Ca_{0.25}$ $(Mg,Fe)_3$ $(Si,Al)_4O_{10}(OH)_2.nH_2O]$; 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 Figure2.
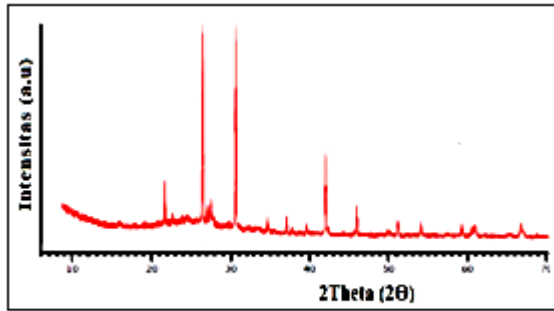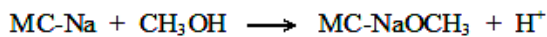

Figure 2. Diffractogram of MC catalyst

Figure2. Diffractogram of MC catalyst

　　　　Based on 2Θ of the results XRD diffractogram of the MC presented in Figure 2and showed that results of modified clay composed of crystalline peaks were sharper and higher than the Clay before modification (Figure 1).The highest peak was 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 zeolite.[22-25]

Result of Transesterification Reaction Using MC,NaN₃/MC, NaN₃/MC, and NaN₃/MCA

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

$$MC\text{-}Na + CH_3OH \longrightarrow MC\text{-}NaOCH_3 + H^+$$

MC catalyst had Na content so that in this reaction $NaOCH_3$ 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 transeterification reaction.When the UCO was inserted into the reactor, $NaOCH_3$ 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. Besides being formed FAME also produced glycerol.In general, the transesterification reaction can take place using heterogeneous catalysts, for example modified clay as a heterogenous catalyst can be written as follows:
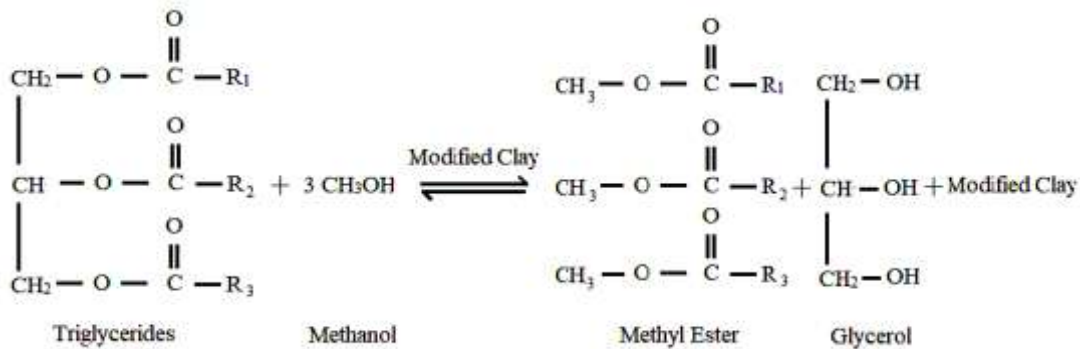

Figure 3. Transesterification reaction using heterogeneous catalyst

The results of the above transesterification reaction is in the form of two layer. The contents of the methyl esters at the top layer, glycerol and catalyst at the bottom layer.Next, the methyl ester and glycerol were separated. Catalyst could easily be separated again because it wassolid. Investigation of the effect of temperature, NaN_3/MCandacetone (NaN_3/MCA catalyst) on the transesterification of UCO has been carried out. The following Table 1 is the results of transesterification of UCO using MC, NaN_3/MC catalys (the amount of NaN_3 was 5% in the MC), NaN_3/MCAcatalyst. The amount of catalyst, methanol and UCO was made the same.

Table 1. Yield of Transesterification of UCO Using MC, NaN_3/MC, NaN_3/MCA

Temperature of reaction (°C)	type of catalyst	Amount ratio of Aceton to Metanol	Weight of UCO (g)	Yield of transesterification product (wt %)
60	MC	--	30	41.5
60	NaN_3/MC	--	30	65.3
60	NaN_3/MCA	2 : 1	30	82.7
65	NaN_3/MCA	2 : 1	30	94.4

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.

In Table 1,at the reaction temperature of 60 °C , using MC catalyst, methyl ester produced far less than treatment with other catalysts. From these results it could be argued that the reaction temperature by using methanol lead to results far from the maximum (only 41 wt%).The maximum temperature for the transesterification process is the temperature almost close to or equal to the boiling point of methanol[26]. The methanol boiling point is 64.7 °C.Furthermore, at the same temperature using a different catalyst, namely NaN_3/MC catalyst, the results of transesterification obtained higher methyl ester (65.3 wt%) than the MC catalyst. This could be caused by the basic properties of this catalyst increase due to the addition of Na metaland it was also possible because of the free electron pair of nitrogen.The next treatment was still at the same temperature (60 °C). In the reaction of the transesterification process using NaN_3/MCA catalyst (the catalyst added acetone with a ratio of methanol to acetone was 1: 2).Acetone functions as a co-solvent. 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-solvent[19].

From the transesterification reaction using NaN_3/MCA catalyst, methyl esters were obtained at 82.7 wt%. Thus the addition of acetone has succeeded in increasing methyl esters in biodiesel synthesis.The following attempted transesterification reaction of UCO at temperature of 65 ° C using NaN_3/MCA catalyst and yield of methyl ester was 94.4 wt %.

The temperature was used quite optimal for producing methyl esters.If the reaction was carried out past this temperature in the transesterification process, the solubility decreases because the dissolution process is exothermic. The formation of biodiesel is always exothermic. The increase in temperature beyond the boiling point of methanol makes it easier for gas molecules to separate themselves and to evaporate leaving the solvent. So that the transesterification reaction becomes less optimal. The increase in temperature reaction results in a decrease in the yield of biodiesel because methanol is lost due to evaporation after the temperature exceeds 65 °C. Adding temperature beyond this point reduces yield due to evaporation of methanol. Several researchers[27-29] have reported that increase in temperature influence transesterificationin a positive manner, however, the temperaturemust not exceed the boiling point of the reacting alcohol toprevent the volatilization of the alcohol during transesterification. The yield of FAME was determined via GC-MS analysis. The GC-MS obtained data of FAMEcomposition in biodiesel.

Next to see the methyl esters produced can be seen in Figure 4, as well as in Table 2, 3, 4 and 5 below.

Figure 4 below is the chromatogram resulting from the transesterification reaction of UCO using MC in variation of reaction temperature.
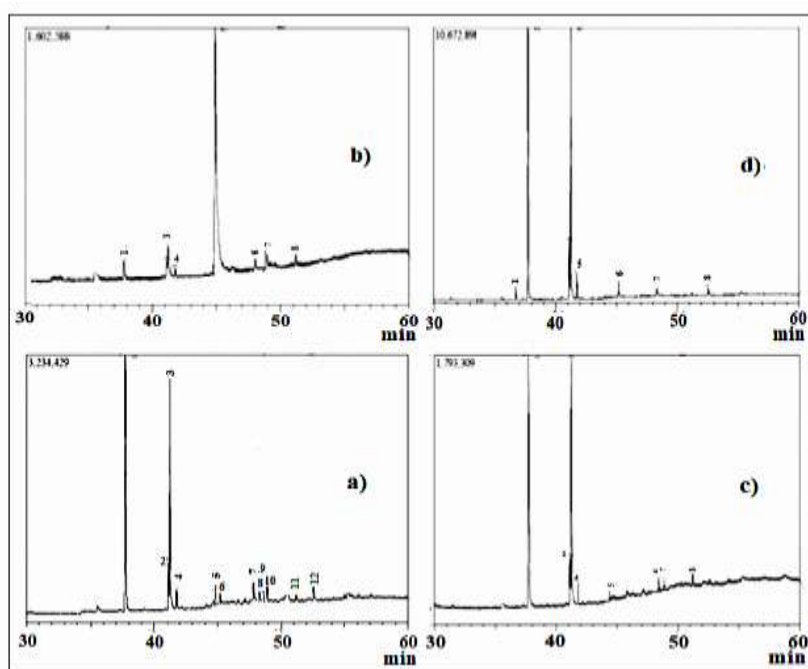
Figure 4. GC-MS chromatogram results of transesterification of UCO
  a) MC catalyst at 60°C   b) NaN₃/MC catalyst at 60°C
  c) NaN₃/MCA at 60°C   d) NaN₃/MCA at 65°C

From Figure 4, there were differences in the results of the transesterification reaction between the catalyst and 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 12 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 UCO using MC catalyst at 60 °C

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	37.739	Hexadecanoic acid, methyl ester	34.65
2	41.134	9,12 hexadecanoic acid, methyl	13.87
3	41.256	10-Octadecenoic acid, methyl ester	23.43
4	41.758	Octadecanoic acid, methyl ester	1.68
5	44.909	Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	5.93
6	45.167	Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester	3.15
7	47.979	13-Octadecenal	6.78
8	48.242	6-Tridecanol	2.65
9	48.386	Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	2.86
10	48.895	Di-n-octyl phthalate	1.52
11	51.208	10-Nonadecanon	0.59
12	52.581	Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester	1.66

The dominant methyl esters (FAME) were Hexadecanoic acid, methyl ($C_{17}H_{34}O_2$)that content of 34.65 %; 10-Octadecenoic acid methyl ester($C_{19}H_{36}O_2$)that content of23.43 %; and 9,12 hexadecanoic acid, methyl ester ($C_{19}H_{34}O_2$) that content of13.87 % respectively.Furthermore, in Figure 4b, there weremany fatty acids with peak numberfewer.Based on the chromatogram, there were 8 retention time detectedwith chemical constituents that were different. The retention time with the resulting compound found in Table 3.

Table 3. Yield of transesterification of UCO using NaN$_3$/MC catalyst at 60 °C

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	37.792	Hexadecanoic acid, methyl ester	4.86
2	41.157	9,12-Hexadecadienoic acid, methyl ester	3.20
3	41.267	10-Octadecenoic acid, methyl ester	11.93
4	41.783	Hexadecanoic acid, methyl ester	2.06
5	44.884	10-Undecenoic acid, methyl ester	66.35
6	48.014	9-Octadecanone	3.89
7	48.895	Di-n-octyl phthalate	5.44
8	51.211	10-Nonadecanone	1.81

The dominant methyl esters (FAME) were10-Undecenoic acid, methyl ester ($C_{12}H_{22}O_2$)that content of 66.35 %; 10-Octadecenoic acid methyl ester($C_{19}H_{36}O_2$)that content of11.93 %; and 9,12 Hexadecanoic acid, methyl ester ($C_{19}H_{34}O_2$)that content of4.86 % respectively.

In Figure 4c, based on the chromatogram, there were 8 retention time detectedwith chemical constituents that were different.The retention time with the resulting compound found in Table 4.

Table 4. Yield of transesterification of UCO using NaN$_3$/MCA catalyst at 60 °C

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	37.727	Hexadecanoic acid, methyl ester	44.65
2	41.129	9,12-Octadecadienoic acid, methyl	7.13
3	41.242	10-Octadecenoic acid, methyl ester	39.87
4	41.750	Octadecanoic acid, methyl ester	3.94
5	44.083	Hexadecanoic acid, 2,3-dihydroxypropyl ester	0.94
6	48.380	Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester	1.82
7	48.886	Di-n-octyl phthalate	1.35
8	51.197	9-Octadecanone	0.30

The dominant methyl esters (FAME) wereHexadecanoic acid, methyl ester($C_{17}H_{34}O_2$)that content of 44.65 %; 10-Octadecenoic acid, methyl ester($C_{19}H_{36}O_2$) that content of 39.87 %; and 19,12-Octadecenoic acid, methyl ester($C_{19}H_{34}O_2$)that content of 7.13 %respectively.

Next, in Figure 4d, based on the chromatogram, there were 8 retention time detectedwith chemical constituents that were different.The retention time with the resulting compound found in Table 5.

Table 5. Yield of transesterification of UCO using NaN₃/MCA catalyst at 65 °C

No.	Retention time (min)	Chemical constituents	Area percentage (%)
1	36.894	Isocyanic acid, octadecyl ester	0.66
2	37.743	Hexadecanoic acid, methyl ester	44.97
3	41.128	9,12-Hexadecadienoic acid, methyl ester	14.67
4	41.262	10-Octadecenoic acid, methyl ester	33.16.
5	41.749	Octadecanoic acid, methyl ester	4.52
6	45.144	Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester	1.05
7	48.381	Oxiraneundecanoic acid, 3-pentyl-, methyl ester,	0.41
8	52.563	Oleic acid, hexyl ester	0.56

The dominant methyl esters(FAME) wereHexadecanoic acid, methyl ester($C_{17}H_{34} O_2$) that content of44.97 %; 10-Octadecenoic acid, methyl ester($C_{19}H_{36}O_2$)that content of 33.16 %; and 9,12-Hexadecadienoic acid, methyl ester ($C_{19}H_{34}O_2$)that content of14.67 respectively.

From Figure 4 a, c and d, and pay attention to Tables 2, 3, 4 and 5, each catalyst produced by the dominant fraction is almost the same. The transesterification reaction of UCO using NaN₃/MC catalyst at a temperature of 60 °C resulted methyl esters of 65.3 wt%.Furthermore, after adding acetone to the same treatment, the resulting methyl ester was 82.7 wt%.This indicates that aceton can increase the yield of methyl esters in addition to increasing the temperature of the transesterification reaction.However, the temperature of transesterification must consider the type of alcohol used.Addition of acetone can increase the solubility of triglycerides with methanol, so thatresult inthe formation of methyl esters.The transesterification reaction of UCO at a temperature of 65 ° C using NaN₃/MC catalyst and acetone produced the highest content of methyl esters or biodiesel that was equal to 94.4 wt%.The dominant methyl esters(FAME) were Hexadecanoic acid, methyl ester($C_{17} H_{34} O_2$) that content of44.97 %; 10-Octadecenoic acid, methyl ester($C_{19}H_{36}O_2$)that content of 33.16 %; and 9,12-Hexadecadienoic acid, methyl ester ($C_{19}H_{34}O_2$)that content of14.67 respectively. The catalytic reaction of transesterification at 60 °C did not run optimally because the temperature has not yet approached the boiling point of methanol.

Conclusion

Modification of Merauke clay with Si/Al Rasio 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 used cooking oil into biodiesel.

In this study, the transesterification of used cooking oil using NaN3/MC could increase the amount of yield of methyl esters (FAME) compared to modified clay (MC) catalysts at the same temperature. The transesterification of used cooking oil using NaN₃/MC could increase the amount of methyl esters produced compared to modified clay catalysts at the same temperature.Furthermore, transesterification of used cooking oil using NaN₃/MC catalyst and added acetone as co-solvent can increase the amount of methyl esters produced at the same temperature compared to NaN₃/MC catalyst without the addition of acetone. Highest conversion into methyl ester was 94.4 wt % which was obtained at temperature of 65 °C using NaN₃/MC catalyst by added acetone as co-solvent.Yield methyl esters (FAME) which dominant were Hexadecanoic acid, methyl ester ($C_{17} H_{34} O_2$) ; 10-Octadecenoic acid, methyl ester($C_{19}H_{36}O_2$) and 9,12-Hexadecadienoic acid, methyl ester ($C_{19}H_{34}O_2$) respectively.

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