

## Modification of Clay Through and Without Fusion Treatment for Catalyst of Biodiesel Synthesis From Used Cooking Oil

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**Abstract :** Transesterification of used cooking oil into biodiesel has been done using modification of clay to zeolite with Si/Al ratio of 5,5 catalyst through and without fusion treatments. The modified clay catalyst without fusion was synthesized by destructing or dealumination of clay with 8M HCl solution, then followed by treating with NaOH, AlCl<sub>3</sub>.6H<sub>2</sub>O, CTAB and distilled water. Meanwhile, modified clay catalyst through fusion was synthesized by dealumination also carried out like the treatment above, then NaOH pellet (NaOH/zeolite ratio = 0.8), followed by treating with AlCl<sub>3</sub>.6H<sub>2</sub>O, CTAB and distilled water. Each of the mixture was regulated to pH of 11.5. Next, and each of the mixture was then poured into a reactor for hydrothermal process at 140 °C for 72 h. The results of the dealumination of clay was characterized by X-ray Fluorescence and the synthesized zeolite was characterized using X-Ray Diffraction. The transesterification of used cooking oil into biodiesel process was carried out in the variation of reaction time process of 1.5, 3, 4.5 and 6 h.

The temperature of reaction of 65°C, and ratio of catalyst : used cooking oil : methanol was 1.0 : 20.0 : 13.3. The main liquid product of transesterification was methyl ester and it was analyzed using Gas Chromatography Mass Spectrometer. The result showed that the dealumination of clay had Si content of 34.77% and Al content of 5.67%. The results of measurements with XRD produced a different form of chromatogram and type of zeolite. The results of transesterification used cooking oil into biodiesel without fusion treatment was 10 wt %, meanwhile the zeolite through fusion treatment was 85 wt %.

**Keywords :** clay, modification, zeolite, transesterification, used cooking oil, 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<sup>1</sup>. Even though the results of repeated cooking (used cooking oil) not suitable for use 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 frying which is generated daily from various sources comprising households, restaurants, catering establishments, and industrial kitchens<sup>2</sup>. Waste cooking oil. 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 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. Catalyst is generally defined as a material that can accelerate chemical reaction into product.

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 has many advantages such as low emissions, biodegradability and better lubricity<sup>3</sup>. 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  $\text{H}_2\text{SO}_4$ , HF,  $\text{H}_3\text{PO}_4$ , HCl and p-toluene sulfonic acid<sup>4-5</sup>. Esterification is normally carried out in a homogeneous phase in the presence of acid catalysts such as  $\text{H}_2\text{SO}_4$ , HF,  $\text{H}_3\text{PO}_4$ , HCl<sup>4-5</sup>. In the esterification reaction produces biodiesel and water<sup>6</sup>. Transesterification reaction can be done in a homogeneous phase in the presence of base catalyst such as NaOH, KOH. Moreover, these catalysts are hazardous and corrosive liquid acids<sup>5</sup>. 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, as in the case of Lewis acid catalyst. 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<sup>7</sup>.

One of heterogeneous catalyst is zeolite<sup>8-11</sup>. Zeolite have been widely used as industrial heterogeneous catalyst because they are inexpensive and environmentally benign. They offer generous surface area and high porosity<sup>12</sup>. The advantage of using heterogeneous catalyst like zeolite is that it can be used repeatedly and easier to separate than the homogeneous catalyst treatment.

Zeolite is porous solid composed of silica and alumina framework that can be used as support. Thus, the basic ingredients for zeolite synthesis are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  which can be obtained from clay, for example from Merauke clay in Merauke District Papua Province, Indonesia. Mineral content of clay can also differ from one place to another where the clay is. The content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in clay is still fused in a chemically bound framework.

Clay also has silica content ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) that is still fused and chemically bonded in the clay. 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<sup>13,14,15</sup>. 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<sup>16</sup>.

## Experimental

### Materials

Clay was obtained from Merauke, Papua Province, Indonesia. The chemicals used were HCl 37%, NaOH pellet,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 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. Used cooking oil which come from palm oil was purchased from a restaurantsuper market in Jayapura.

### Instrumentation

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

### Procedure

#### Synthesis of modified clay Through and Without Fusion Treatment

After being washed and separated with water then dried in oven at temperature of 120 °Cfor 4 h, the clay was grinded and sieved (100 mesh). The clay (50 g) was destructed using 100 mL of 8M HCl at 100°C followed with refluxing mixture for 6 h. The clay was filtered and washed using deionized aquadest until neutral condition, dried on the oven at 120 °C for 4 h. Furthermore, synthesis without fusion treatment was carried out (LTF3) as follows:

Dealuminated clay (10 g) was mixed with NaOH (0.8 g),  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (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 synthesis through fusion was also done (LF3) as follows :

The clay results of dealumination was fused withNaOH 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 two samples of 2treatments were done hydrothermally treated at 140°C for 72 h. The synthesized zeolite 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, used cooking oil (UCO) was absorbed first with zeolite synthesized without fusion treatment. Then, 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 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 putUCO (30 g) while stirring, the temperature was increased to 65 °C for 6 h. Transesterification process was also carried out with reaction time of 1.5 ; 3 and 4.5 h. After completion of the reaction, the mixture was cooled then separated between solid fraction (catalyst) and the liquid fraction in the form of mehtyl 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 estes was analyzed using GC-MS. The conversion was calculated by following formula:

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

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

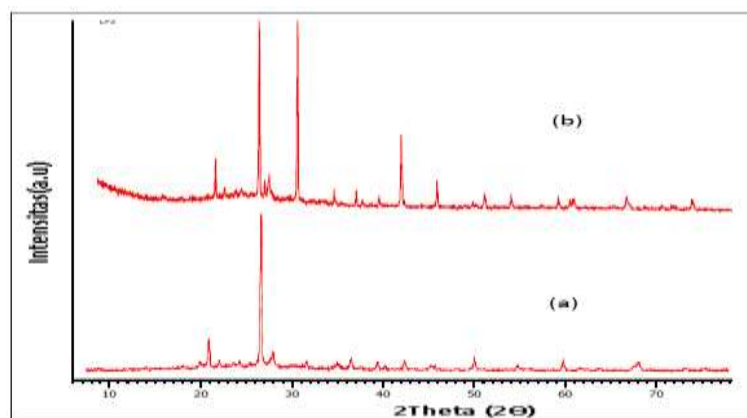
W2 = methyl ester product weight (g)

## 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 = 5.5, 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. 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  $\text{Fe}^{2+}$ ,  $\text{Mn}^{+}$  in the contents of clay. However, interaction with 8M HCl, in certain clay zeolites 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 = 34.77% and Al = 5.67%.

### Results of Analyze of LTF/3 and LF3 Catalyst Using X-Ray Diffraction (XRD)



**Fig.1. Diffractogram of a) LTF3, b) LF3**

Base on JCPDS (2004) Joint Committee on Powder Diffraction Standards, the XRD results in Fig. 1a showed that the LTF3 was composed of various minerals which showed heterogeneity implies. Impurities contained in the LTF3 still higher. Base on  $2\theta$  the results of the diffractogram were 20.74,  $d = 4.28$  (quartz); 26.55,  $d = 3.35$  (gismondine); 27.75,  $d = 3.21$  (mordenite); 36.43,  $d = 3.19$  (mordenite); 39.36,  $d = 2.28$  (mordenite); 45.36,  $d = 1.99$  (sodalite); 50.06,  $d = 1.82$  (sodalite); 59.88,  $d = 1.54$  (mordenite) respectively.

The mineral content of LTF3 results of synthesis without fusion treatment from raw materials of Merauke Clay based on  $2\theta$  include: gismondine, mordenite, sodalite and quartz, as well as other amorphous mineral which was quite a lot. The dominant mineral content in the LTF3 based on strong peaks was gismondine zeolite  $[(\text{Na}, \text{Ca}_2, \text{K}_2)_4(\text{Al}_8\text{Si}_8\text{O}_{48}) \cdot 16\text{H}_2\text{O}]$  based on its  $2\theta$ . Furthermore, based on  $2\theta$  of the results XRD diffractogram of the LF3 presented in Fig. 1b showed that result of modified clay composed of crystalline peaks were sharper and higher than the LTF3. The highest peak at  $2\theta = 26.65$ ,  $d = 3.34$ . Base on  $2\theta$  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. The minerals contained in the LTF3 were gismondine, mordenite, sodalite and quartz. Gismondine zeolite was the dominant mineral of the LF3. 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<sup>17-20</sup>.

### Result of transesterification reaction using LTF3 and LF3 catalyst

Table 1 showed results of UCO (used cooking oil) transesterification using LTF3 and LF3 catalyst with various of reaction time.

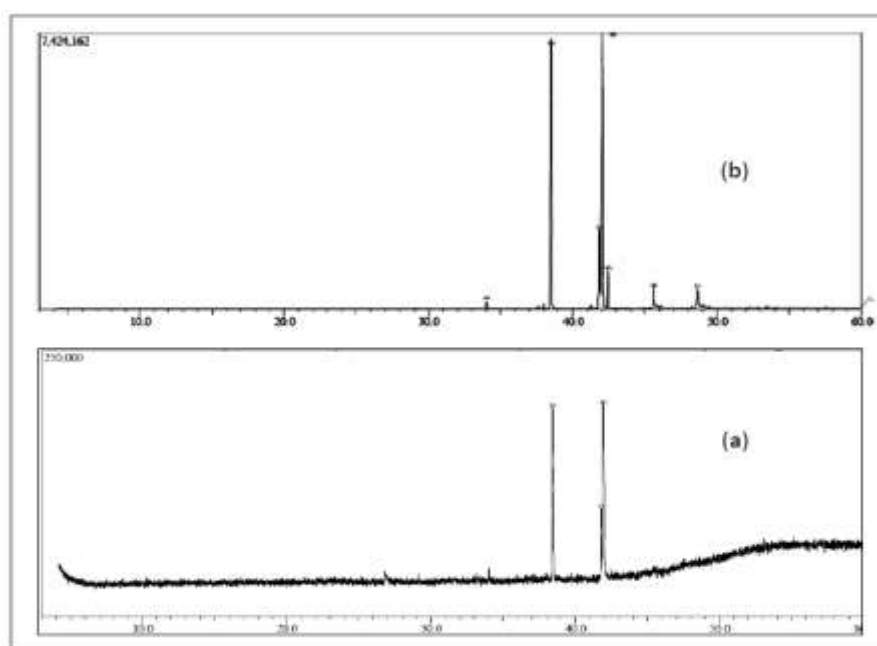
**Table 1. Transesterification results of used cooking oil using LTF3 and LF3 catalyst**

Reaction time (h)	Conversion of UCO to biodiesel using LTF3(wt %)	Conversion of UCO to biodiesel using LF3(wt %)
1.5	-	38
3	3	52
4.5	6	76
6	10	85

From the data in table 1, on heterogeneous catalyst LTF3 where the results of the diffractogram using XRD shows peaks with low crystallinity or possible number of minerals in the form of amorph which was inactive as catalyst. Thus it was possible that the results of the transesterification reaction of used cooking oil using LTF3 catalyst would produce small amount of biodiesel. During the reaction time of 1.5 hours, there was no visible methyl ester produced in this time span. Then after reaction time of the transesterification was increased to 3, 4.5 and 6 h, there has been an increase in the yield of biodiesel. In the reaction time of 6 hours with the same temperature and amount of LTF3 catalyst, the conversion of used cooking oil to biodiesel was 10wt %. Conversely, the transesterification reaction using LF3 catalyst at the same temperature and amount of catalyst as the LTF3 catalyst obtained significant results in the reaction time of 1.5, 3, 4.5 and 6 h. Conversion to biodiesel at reaction time of 1.5; 3; 4.5 and 6 hours were in 38, 53, 78 and 85 wt % respectively.

The significant difference in results obtained from these two types of catalysts (LTF3 and LF3) because the LF3 catalyst based on the results of the diffractogram that showed lower amorph content than the LTF3 catalyst. Amorph content contained in the catalyst will affect the activity of the catalyst. The more amorph content of catalyst material, the more active the catalyst will be reduced so that the result of the transesterification reaction in the form of biodiesel will also be low. In addition, LF3 catalyst was made from pretreatment through fusion with NaOH (pellets), so it can be possible to have more Na donations than LTF3 catalysts that was made without fusion treatment. Due to the presence of more Na, it will affect the conversion to biodiesel.

Figure 2 below is the chromatogram resulting from the transesterification reaction of used cooking oil using LF3 catalyst for 3 and 6 h of reaction time.



**Fig. 2. GC-MS Chromatogram of transesterifikasi product of UCO using LF3 catalyst**  
 a) Reaction time of 3 h b) Reaction time of 6 h

From Figure 2, there are differences in the results of the transesterification reaction between 3 h (a) and 6 h (b) reaction time for used cooking oil derived from palm oil. In the 3 h of transesterification reaction period,

there were many fatty acids whose peak were very low with the main peak detected as much as 3 pieces based on retention time. With reaction time of 3 h, the transesterification reaction was not enough to convert all triglycerides to methyl ester, only 3 methyl esters were obtained based on the analyst with GC-MS. The 3 compounds detected were retention time = 38.448 (octadecanoic acid methyl ester that content of 31.83%); retention time = 41.842 (linoleic acid methyl ester that content of 16.96%) and retention time 41.975 (9-Octadecenoic acid methyl ester that content of 43.21 %) respectively. This methyl ester compound was the dominant product in the transesterification reaction of used cooking oil using LTF3 catalyst with reaction time of 3 h.

Furthermore, in Figure 2b, in the 6 h of transesterification reaction period, there were many fatty acids whose peaks were very high and there were almost no low peaks such as at 3 h of reaction time. From the chromatogram produced, it was seen that there was significant methyl ester produced. Based on the chromatogram, there were 7 retention time detected. The retention time with the resulting compound were retention time = 34.012 (tetradecanoic acid methyl ester that content of 1.03%); retention time = 38.504 (hexadecanoic acid methyl ester that content of 37.61%), retention time = 41.858 (linoleic acid methyl ester that content as much as 10.24%); retention time = 42.043 (11-octadecenoic acid methyl ester that content of 42.20%); retention time = 42.458 (octadecanoic acid methyl ester that content of 4.24 %); retention time = 45.595 (2-hydroxy-1,3-propanediyl ester that content of 2.79 %) and retention time = 48.672 (9-octadecenal that content as much as 2.89%) respectively. Based on the retention time, the transesterification reaction using LF3 catalyst with reaction time of 6 h, the dominant compound was methyl ester of 11-Octadecenoic acid that content of methyl ester as much as 42.20%. From the transesterification reaction for 6 h, it produced methyl ester or biodiesel of 85 wt %.

## Conclusion

Modification of Merauke clay produced synthetic zeolite through dealumination without fusion treatment (LTF3) and dealumination followed by fusion treatment with NaOH pellets (LF3). then the hydrothermal formation reaction for 72 h of 140°C produced zeolites with different crystallinity even though the Si/Al ratio was the same. LTF3 and LF3 produced some types of zeolite minerals, the dominant one was gismondine zeolite. LF3 produced higher crystallinity compared to LTF3 catalysts. The longer the reaction time of transesterification reaction in this study, produced more biodiesel. LTF3 catalyst produced biodiesel of 10 wt% at reaction time of 6 h, while LF3 catalyst produced biodiesel of 85 wt% at the same treatment in the transesterification process.

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