



Enrichment of Sawahlunto Clay with Cation Ca^{2+} and Cu^{2+} and Preliminary Test of its Catalytic Activity in CPO Transesterification Reaction

Lestari Ningsih¹, Aju Deska¹, Syukri Arief¹, Upita Septiani¹, Yulia Eka Putri¹, Mai Efdi², Syukri^{1*}

¹Laboratory of Material Chemistry, University of Andalas, Padang, Indonesia.

²Laboratory of Natural Product Chemistry, University of Andalas, Padang, Indonesia.

Corresponding author email: syukridarajat@sci.unand.ac.id

Received : September 12, 2020

Accepted : December 23, 2020

Online : December 30, 2020

Abstract – This research is aimed to examine the catalytic activity of Sawahlunto clay, which is enriched with Ca^{2+} and Cu^{2+} transesterification of Crude Palm Oil (CPO) to produce biodiesel. Based on the results of the analysis with X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD), Sawahlunto clay consists of about 61% Si and 24% Al with a Si/Al mole ratio of 2.7 and typical clay mineral consisting of kaolinite and illite, another mineral fund was quartz and goethite. The mineral composition changes after calcination, where kaolinite and illite disappeared. Fourier Transform Infrared (FTIR) analysis shows that calcination can remove the organic compounds Sawahlunto clay; thus, the clay was used without calcination for the next step. Clay samples can be enriched with Ca^{2+} ions and Cu^{2+} ions without damaging their mineral composition, where more Cu^{2+} ions are loaded than Ca^{2+} ions. The Sawahlunto clay enriched with Ca^{2+} ions showed a slightly better catalytic activity in the transesterification of crude palm oil (CPO) than its parent clay; when enriched with Cu^{2+} ions, the catalytic activity did not appear at all. However, the homogeneous counterpart of such catalyst, calcium nitrate, was still the most active and selective compared to all others.

Keywords: Clay, Catalyst Heterogeneous, CPO, Transesterification, Biodiesel.

Introduction

Energy demand throughout the year continues to increase in line with the rapid development of the industry. So far, the energy resources utilized are oil, gas, coal, geothermal, and water (Helwani *et al.*, 2009). In energy production, among others, in the manufacture of bioethanol, diesel, and biodiesel. Reaction. It always requires a catalyst as a substance to accelerate the reaction rate in converting reactants into products. Catalysts can be classified into two, namely homogeneous catalysts and heterogeneous catalysts. Catalysts are very important in industry because they can reduce the reaction's activation energy and increase the rate of reaction (Catherine and Alan, 2005).

The importance of catalysts in the chemical production process is around 75% of the process being synthesized with catalysts and even up to 90% of industrial processes. Various organic byproducts to make plastics, synthetic fibers for medicinal materials, dyes, plant protection materials, leather, and synthetic pigments can be obtained through a catalytic process (Suharto, 2010). One example of the use of catalysts is in energy production applications, namely biodiesel fuel. Biodiesel fuel can be sourced from animal and vegetable fats as raw materials. Biodiesel from animal fats and vegetable fats was re-evaluated for fuel for diesel engines because their combustion tends to be cleaner, environmentally friendly, and a form of concern in supporting energy security (Gopinath *et al.*, 2010). In environmentally friendly energy production, a catalyst is needed in its manufacture (Cynthia *et al.*, 2014).

Catalysts can be divided into liquid catalysts (homogeneous) and solid catalysts (heterogeneous). Researchers mostly use heterogeneous catalysts rather than homogeneous catalysts. One of the advantages of using heterogeneous catalysts is that the separation between reactants and products can be done easily (Catherine and Alan, 2005). Among the metal catalysts that have been used for synthesis in biodiesel production with clay support are CaO (Cinthia *et al.*, 2014), Ni-Co (Yusuf *et al.*, 2018), TiO₂ (Amit *et al.*, 2017), Cd- Mn (Mamoon *et al.*, 2019) and polarized Cu (Carmen *et al.*, 2017). In this case, the catalyst used in biodiesel production from vegetable oil is crude palm oil (CPO). Several researchers have researched the use of heterogeneous catalysts from clay in the application of biodiesel production from palm oil, including real West Pasaman clay with a biodiesel yield of 41% (Septioga *et al.*, 2019), lime clay calcined at 450°C for 4 hours, the yield of biodiesel was 8.1% (Nuripati *et al.*, 2019), and Agam original clay by 22% (Putri *et al.*, 2020) and the use of vegetable oil from palm oil can also be used using NaOH catalysts and egg-shells (Agus *et al.*, 2020; Shahanaz *et al.*, 2020). some literature, it is explained that natural clay needs to be modified with a catalyst to increase catalytic activity because the unmodified sample has low catalytic power.

One of the advantages of natural clay is that it is a solid material used as an adsorbent or as a catalytic. In general, clay is used as an adsorbent because it has a higher Si/Al mole ratio while the low Si/Al has the potential as a catalytic such as activation of region cengar natural clay using sulfuric acid, which can increase the value of the Si/Al mole ratio when the concentration is raised (Fiola *et al.*, 2015).

Several researchers have conducted studies on the modification of clay and zeolite, resulting in increased catalytic activity after modification with a catalyst such as the use of KOH/ZrO₂ in bentonite pillared (Yeslia *et al.*, 2018), KOH is supported by West Pasaman clay (Septioga *et al.*, 2019), and NaOH is supported by Lubuk Minturun clay (Ferdian *et al.*, 2019). Clay and zeolite enrichment uses alkali, alkaline earth, and transition metals on the clay support as a material surface provider to make a homogeneous catalyst into a heterogeneous (solid) catalyst.

At this time, the raw materials for biodiesel production can use soybeans, coconut, castor oil, and palm oil so that the triglyceride fatty acid content can be used for biodiesel production. In this reaction, they need a catalyst to accelerate the formation of biodiesel. One use is a heterogeneous catalyst, which can be made with the help of clay as a surface to spread metal cations on the surface evenly. One of the reasons for using clay is that it is easy to obtain, the presence of cations as a catalyst, and has a mole ratio of Si/Al, which is predicted to have different properties to the size of Si and Al in the sample. In this research, Sawahlunto clay was used as a sample of solid material used as a heterogeneous catalyst.

The clay minerals of Sawah Lunto are generally used to manufacture red brick and chili milled stone crafts. So, in this case, the unique properties of clay have encouraged researchers to think about using Sawah Lunto clay as a catalyst support in biodiesel production on a laboratory scale as a preliminary test. Based on the background obtained, the researchers are interested in conducting research studies on the use of Sawahlunto clay as catalyst support.

Materials and Methods

Time and site

This research was conducted at the Laboratory of Materials Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University (Unand), from August 2019 to July 2020. Characterization of clay samples was carried out using X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), X-Ray Diffraction. (XRD), Surface Area Analyzer (SAA)-BET, Atomic Absorption Spectrophotometer (AAS), and Gas Characterization Chromatography-Mass Spectrometry (GC-MS).

Chemical Material

The material used for catalyst preparation is natural clay taken in Sawah Lunto, West Sumatra Province. The materials used are Ca(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O, and water. The raw materials for making methyl esters through transesterification reactions are crude palm oil (CPO) and methanol (CH₃OH).

Tools and Instruments

The equipment used includes; several glasses and ceramic utensils such as condensers, measuring cups, beakers, measuring flasks, measuring pipettes, Erlenmeyer glasses, mortar, pestle, beaker, and others. Then some standard electrical equipment such as analytical scales, ovens, sieves, and magnetic stirrers. For filtering, the ordinary filter paper is used. Furthermore, standard safety equipment such as masks, google, and gloves.

For the characterization of instruments consisting of X-ray Fluorescence (XRF) (*NEXCGRigaku*), X-ray Diffraction (XRD) (*X'Port PAN Analytical*), Fourier Transform Infrared (FTIR) (*Thermo Scientific: Nicolet iS10*), Surface Area Analyzer (SAA)-BET, and Gas Chromatography-Mass Spectrometer (GC-MS) for the analysis of the content of types of compounds from the obtained methyl esters

Sampling

Clay samples were taken from three red brick manufacturing locations in the Sawahlunto area, namely in the Durian clay samples. Clay samples that have not been treated at all are named o-clay (original clay) to facilitate subsequent work.

Clay Sample Preparation

A number of o-clay was heated at 110°C for 4 hours, crushed, and passed through a 180µm sieve. In this study, to facilitate the work, the heated clay was named h-clay (heated clay), then the h-clay was characterized by XRF, XRD, FTIR, and SAA-BET

Clay Thermal Activation

h-clay is suspended in distilled water. Then centrifuged for 15 min at 3000 rpm, the precipitate was separated and dried at 110°C for 2 hours. The clay was crushed and heated again at 150°C for 2 hours and cooled. A total of 100 grams were calcined at 700°C for 8 hours. Then crushed and sieved with a size of 180 µm and given the name c/h-clay (calcinated heated clay), which was further characterized by XRF, XRD, FTIR, and SAA-BET.

Ca²⁺ and Cu²⁺ Catalyst with Clay Support

An amount of 20 g h-clay was washed with distilled water and suspended for 24 hours at room temperature, and filtered. Then separate the precipitate with a solution. Then the sample was dried at 110°C and then crushed. The samples were then re-oven at 150°C for 2 hours. Then the sample was crushed and sieved 180 µm. The composition used in mixing 20 g h-clay and 100 mL Ca(NO₃)₂·4H₂O. The mixture is filtered with filter paper, then heated to remove moisture at a temperature of 110°C. The mixture was labeled Ca/h-clay and continued with characterization with XRD and the filtrate was measured using AAS. the same thing was done using a Cu(NO₃)₂·3H₂O catalyst and then the sample was named Cu/h-clay.

Test of Catalyst Activity in Transesterification of CPO

The transesterification of crude palm oil (CPO) samples (which contain triglycerides) into biodiesel (methyl ester) is carried out in a 250 mL three-neck flask connected to a condenser for reflux, equipped with a temperature indicator mounted on top of the hotplate magnetic stirrer. The reaction procedure is as follows: For reaction stoichiometry, the molar ratio of palm oil and methanol used in this study is 1:6, and the amount of catalyst used is 5% by weight of palm oil. Initially, the catalyst and methanol were heated to 50°C under continuous stirring. Next, 100mL of palm oil was added to the three-neck flask, which had previously been heated at 110°C until there were no more water bubbles remaining, then the temperature was allowed to drop to 50°C. The catalyst, methanol, and palm oil are mixed. The transesterification reaction was carried out for 4 hours at 65°C with a stirrer 750 rpm, stirring. At the end of the reaction, the flask is cooled to room temperature, and the catalyst is separated from the product mixture using filter paper. The biodiesel product is separated from the glycerol using a separating funnel. The biodiesel is washed with hot distilled water (50°C) with a volume of 1:1 and pulverized for 5 min to form a white liquid. Let the mixture sit so that the water collects at the bottom. Biodiesel is heated at a temperature above the boiling point of water (110°C) until there are no more water bubbles. The main chemical components contained in the product were analyzed by GC-MS. To calculate the amount of yield produced, we use the formula below:

$$\text{Rendemen (\%)} = \frac{\text{Top Layer Product} \times \% \text{FAME}}{\text{CPO mass used}} \times 100 \% \quad (1)$$

Noted : CPO=crude palm oil FAME= fatty Acid Methyl Ester

Result

Parameters Properties Clay

Based on the observed parameters, the physical and chemical properties of clay can be observed through, as follow: changes in composition, changes in sample color, changes in the FTIR spectrum that have been analyzed, and the stability of clay mineral crystals. Some of the characteristics of clay that are good for use as

heterogeneous catalysts are the Si/Al ratio, the elemental composition of the cations in the clay, the type of mineral crystals, the bonds formed, and the surface area of the clay. The capacity analyst characteristics were analyzed to determine the elemental composition, Si/Al mole ratio, type of crystal, surface area, load capacity, and catalytic activity as a preliminary study of Sawahlunto clay.

Effects of Calcination

Characteristic of clay color

The h-clay sample was calcined at 700°C to see its effect on physical color, Si/Al mole ratio, infrared absorption band, crystallinity, and surface area. We can see in Fig 1 that the calcination gives only a slight color change from dark brown to light brown.

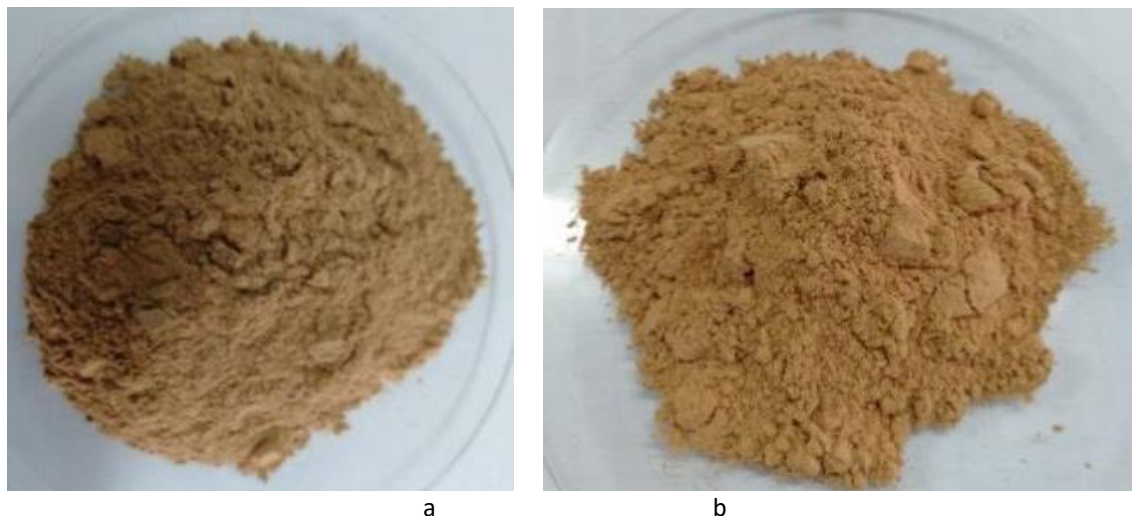


Figure 1. Different color of clay a). h-clay samples before calcination and b). c/h-clay samples after calcination

Analysis with XRF

XRF is a tool used to analyze the elemental composition of a compound contained in a sample using the spectrophotometric method. The difference in the number of elements in the clay can be shown in Table 1.

Table 1 Data on the results of measurements of h-clay and c/h-clay with XRF

Element	h-clay (%)	c/h-clay(%)
Si	61.49	60.51
Al	23.73	21.58
Si/Al	2.7	2.9

Analysis with FTIR

One of the studies of clay mineralogy is by using infrared spectroscopy. The infrared absorption spectrum of a mineral has a distinctive band. This spectroscopic analysis is carried out to determine the types of vibrations between the atoms in the clay mineral. The analysis is carried out in the area of wave number 400-4000 cm^{-1} because usually, the characteristics will appear in the wavelength area.

Analysis with XRD

From XRD analysis, it can be explained that the h-clay is dominated by quartz minerals at an angle of $2\theta:26^\circ$, with the highest intensity, as can be seen in Fig 3.

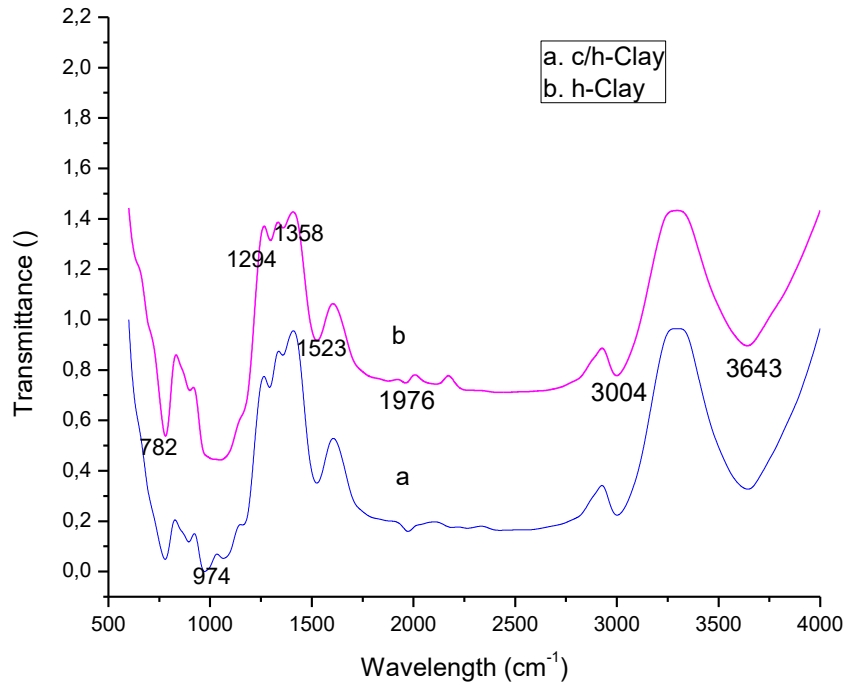


Figure 2. Spektrum FTIR sample a) h-clay and b). c/h-clay

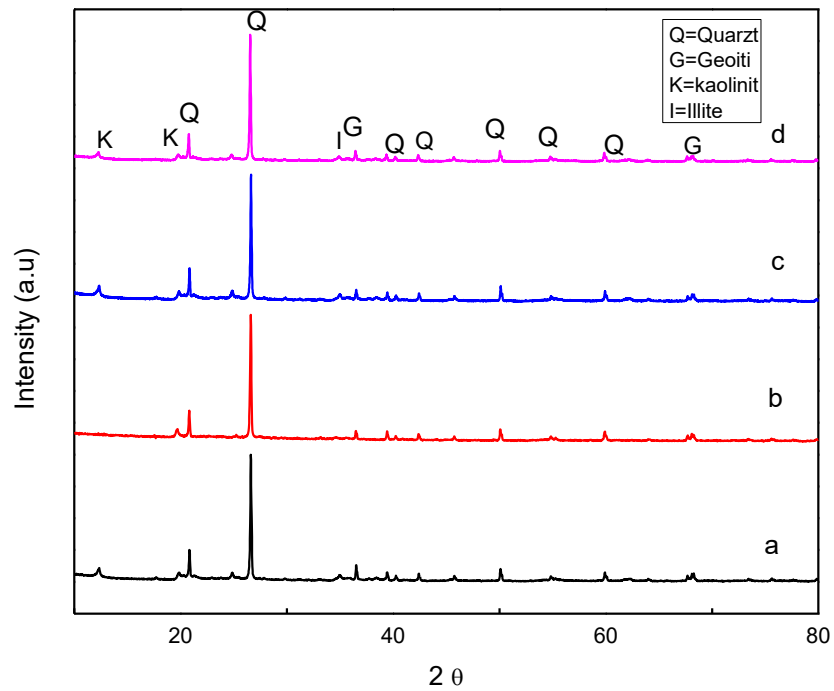


Figure 3. Spectrum XRD of 4 samples a). XRD analysis of h-clay samples, b). c/h-clay samples, c). Ca/h-clay samples, and d. Cu/h-clay samples

Analysis with SAA-BET

Based on the data from SAA measurement results for h-clay and c/h-clay, as shown in Table 2, it can be concluded that heating to a temperature of 700°C increases the specific surface area. This is a phenomenon that usually occurs in natural materials that are dominated by quartz, where the higher the heating temperature is given, the particles tend to break down into smaller pieces. If this natural material is dominated by clay minerals such as kaolinite, illite, or montmorillonite, heating actually makes the number of layers increase, thereby reducing its specific surface area.

Table 2. Surface area of h-clay and c/h-clay samples from each region.

Material	Surface area (m ² /g)
h-clay	32.68
c/h-clay	35.17

Measurement with AAS

Measurements with AAS were carried out to determine the number of Ca²⁺ and Cu²⁺ cations that can enrich the clay, and based on the measurement results obtained, the fact that Cu²⁺ ions are more loaded by clay than Ca²⁺ ions.

Table 3. The load capacity of h-clay against Ca²⁺ and Cu²⁺ cations.

No	Metal	Capacity (% m/m)	
		Room Temperature	70 °C
1	Cu/h-clay	5.76	5.3
2	Ca/h-clay	2.73	1.95

Discussion

Elemental Analysis

Elemental analysis is based on qualitative and quantitative methods to determine the cations from the clay samples which are used as catalysts. Based on the analysis of the XRF measurement results, it can be seen that the Sawahlunto clay sample is dominated by silica and alumina, which characterizes natural clay (Wahyu *et al.*, 2004) with a Si/Al mole ratio of 2.7. We also conclude that calcination at 700 °C against the clay with the code name h-clay has a significant effect on the Si/Al mole ratio (Table 1) because this clay sample is used as a catalyst so the low Si/Al mole ratio will be better because of the increase. Alumina content means that there is a lot of negativity that can contain the active catalytic center, which is usually metal ions or protons. On the other hand, the increase in the Si/Al mole ratio is about 7%, so that it can increase the number of pores and increase the specific surface area of the clay sample (Gil *et al.*, 2005). This happens because the clay will be used more as a catalyst than as an adsorbent. It can be concluded that calcination does not need to be done again for the next processing stage.

Bond Analysis

FTIR instrument is used to recognize molecular structures, especially chemical bonding, and functional groups. Based on the analysis (Figure 2), it can be seen that calcination at 700°C does not have a significant effect on the absorption pattern of infrared rays. However, while bands at 694 and 795 cm⁻¹ are due to the Si-O stretching, between 1000 and 1250 cm⁻¹, there is a slight difference where there is a vibration of the band at 1031 cm⁻¹ is attributed to the (Si-O) planar stretching (Abdul *et al.*, 2017), which is predicted to come from humus compounds that are still present in the h-clay sample which is then no longer visible after calcination at 700°C. c/h-clay has more hydroxyl groups than h-clay, which can be seen from the increase in the intensity of the absorption band around 3000 cm⁻¹ as a result of the stretching vibration of the O-H group and around 1500 cm⁻¹, which is the bending vibration of H-O-H. FTIR spectrum can be seen in Fig 2.

The increase in iron content from c/h-clay is as shown in XRF data (Table 1) and can also be confirmed from the IR c/h-clay spectrum with the stronger intensity of Fe-OH stretching vibration peaks in the c/h-clay sample around 750 cm⁻¹. From the IR spectra of h-clay and c/h-clay, we can conclude that the heating process at 700°C does not have a significant effect on the absorption pattern of clay in the IR region.

Crystal Structure Analysis

In the XRD analysis also found two typical clay minerals, namely kaolinite and illite, were also found although with low intensity; the other mineral is goethite. It can be said that the soil samples taken in Sawahlunto were dominated by quartz with not too high clay content. After heating h-clay to a temperature of 700°C for 8 hours, it was found that the mineral composition and crystal structure of the Sawahlunto clay (labeled c/h-clay) was still dominated by quartz but kaolinite and illite minerals no longer appeared. This gives the conclusion that heating to a temperature of 700°C actually has a negative effect on the presence of clay minerals from the types of kaolinite and illite. So as explained in the previous section, clay in the form of h-clay is used for further processing, where in Fig 3c and 3d it can be seen that the enrichment of h-clay with Ca^{2+} and Cu^{2+} ions does not provide significant changes to the stability and crystalline composition of the parent clay. This property is very important because clay can act as a heterogeneous catalyst and catalyst support at the same time where structural stability is very important.

Loading Capacity Analysis

Based on the analysis of the load capacity of Ca and Cu catalysts with AAS, the percentage of Cu^{2+} is more heavily loaded than Ca^{2+} ions, which is in accordance with the theory that the radius of Cu^{2+} ions is relatively smaller than the radius of Ca^{2+} ions so that it is easier to enter the pores and clay-layered structures (Catherine E. H and Alan G. S., 2005). Another thing that was observed was that clay enrichment was easier to carry out at room temperature than at higher temperatures. Thus, clay can be used as a heterogeneous catalyst in a catalytic test.

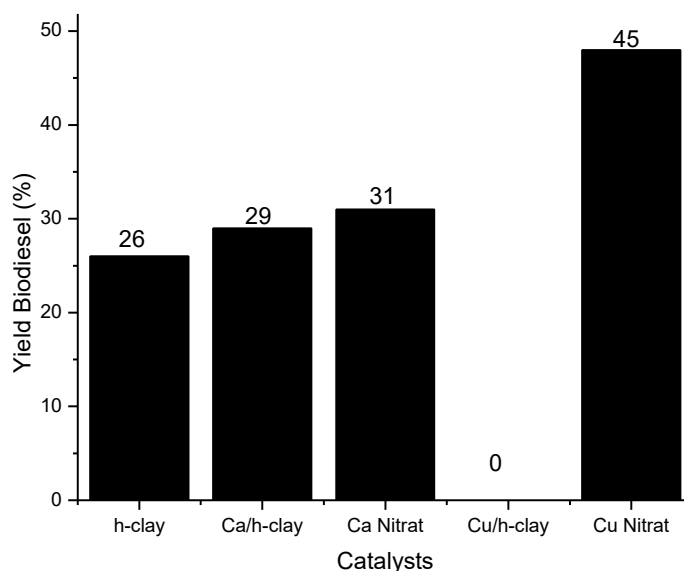


Figure 4. Results of the methyl ester product with five types of catalyst

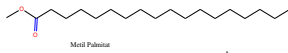
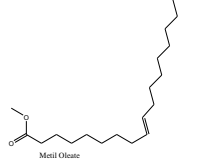
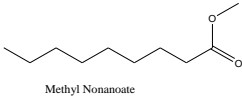
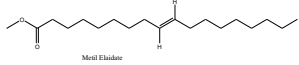
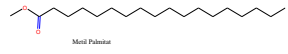
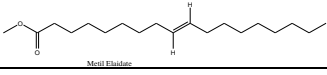
Catalytic Activity Test

GC-MS is used for qualitative and quantitative identification of the individual components in the compound mixture, and in this study, it is used to measure the methyl ester content of the CPO transesterification reaction, where the transesterification product consists of methyl ester and glycerol. The catalytic activity test of the Sawahlunto clay in the transesterification reaction of CPO to obtain methyl ester was carried out by comparing the performance of five catalysts; on five types of catalysts, namely three heterogeneous catalysts (h-clay, Cu/h-clay, and Ca/h-clay) and two homogeneous catalysts (Cu-nitrate and Ca-nitrate). The reaction conditions for the five catalysts were made the same, namely the reaction time of 4

hours, the reaction temperature of 65°C, the speed of 500 rpm, the ratio of the weight of the catalyst to oil is 5%, and the mole ratio of CPO to methanol is 1:6. Comparison of yields in the form of yield and types of methyl ester compounds is shown in Table 4. In general, it can be concluded that under the same reaction conditions, the homogeneous catalyst group gives a relatively higher yield than the equivalent heterogeneous catalyst. The enrichment process of Sawahlunto clay with Ca²⁺ ions only increases the catalytic activity by about 106%, while those enriched with Cu²⁺ ions actually lose their catalytic activity altogether.

The XRF and XRD analysis results described in the previous section can be used as an argument for why the catalytic activity of h-clay and Ca/h-clay is not too high because most of these clays contain more quartz minerals than typical clay minerals such as montmorillonite, kaolinite, and illite. Theoretically, if the clay mineral content is higher, the catalytic activity will also increase, whereas if the quartz mineral is dominant, then the material is more suitable for use as an absorbent. The weak bond between the cations attached to the Sawahlunto clay due to quartz dominance causes its catalytic activity to be not too high.

Table 4. Results of the methyl ester product from the CPO transesterification reaction.

Catalyst	Yield Methyl Ester (%)	Methyl Ester	Molecular Formula	Structure	Comparison methyl ester Saturated & Unsaturated
Cu-Nitrate	25	Methyl Palmitate	C17H34O2		51:48
	23	Methyl oleate	C19H36O2		
Ca-Nitrate	31	Methyl Nonanoate	C10H20O2		100
Ca/h-clay	12	Methyl Stearate	C19H38O2		41:59
	17	Methyl Elaidate	C19H36O2		
h-clay	15	Methyl Palmitate	C17H34O2		58:42
	11	Methyl Elaidate	C19H36O2		

When viewed from the side of selectivity, Ca-nitrate is the most selective because it only produces one type of methyl ester, namely nonanoic acid methyl ester. If Cu-nitrate gives equal saturated and unsaturated methyl esters, then h-clay and Ca/h-clay produce two types of methyl esters (saturated and unsaturated) with a slightly larger percentage of unsaturated. Saturated chain methyl esters are preferred by diesel engines over unsaturated chains because they have a lower density with a greater viscosity (Gopinath *et al.*, 2010).

Conclusion

Sawahlunto clay has been enriched with Ca²⁺ and Cu²⁺ as a heterogeneous catalyst for the transesterification reaction process of CPO with methanol to produce biodiesel. Based on XRF and XRD analysis results, Sawahlunto clay has a Si/Al mole ratio of 2.7 with a typical clay mineral content consisting of kaolinite and illite minerals, where another non-clay mineral was quartz with the most dominant portion. Sawahlunto clay binds more Cu²⁺ ions than Ca²⁺ ions, and the enrichment process is better done at room temperature.

Sawahlunto clay enriched with Ca^{2+} ions showed slightly better catalytic activity compared to its parent clay, where the unsaturated methyl ester was also slightly preferred over saturated one. However, the clays enriched with Cu^{2+} ions showed no catalytic activity. Among all catalysts tested at the same reaction condition, their homogeneous counterpart, Ca-nitrate, was still the best in terms of activity and selectivity.

Nomenclature

h-clay	= heated clay
c/h-clay	= calcinated/heated clay
Ca/h-clay	= Calcium/heated clay
Cu/h-clay	= Copper/heated clay
CPO	= Crude palm Oil
XRF	= X-Ray Fluorescence
XRD	= X-Ray Difrraction
FTIR	= Fourier Transform Infrared
AAS	= Atomic absorption spectroscopy
SAA	= Surface Area Analyzer
GC-MS	= Gas Chromatography-Mass Spectroscopy

Acknowledgment

We want to thank LP2M Universitas Andalas, who have supported this research financially through the 2019 Budget Year Research Grant Funds with a Contract No.T/60/UN.16.17/PP.15-KRP2GB/LPPM/2019.

References

- A.Gil, M.A., Vicenteb, S.A. and Korili. 2005. Effect of the Si/Al ratio on the structure and surface properties of silica-alumina-pillared clays. *Journal of Catalysis*, 229:119–126.
- A.Gopinath., Puhana, S. and G. Nagarajan. 2010. Effect of unsaturated fatty acid esters of biodiesel fuels on combustion, performance and emission characteristics of a DI diesel engine. *International Journal of energy and environment.*, 1(3):411-430. Journal homepage: www.IJEE.IEEFoundation.org
- Abdu, R Y., Ahmed M.S.M. 2017. Sudanese Clays for Heterogeneous Methanolysis of Castor Oil. *Journal of Chemistry and Biochemistry*, 5(2):1-9.
- Agus, H., Amieria, CG. Tri, WS. and Mareli, T. 2020. First order kinetics of biodiesel synthesis using used frying oil through transesterification reaction., *Aceb Int. J. Sci. Technol*, 9(1):1-11.
doi: 10.13170/aijst.9.1.13297
- Amit, M., Akansha, M. Manisha, S. and Soumen, B. 2017. Enhanced heterogeneous photodegradation of VOC and dye using microwave synthesized TiO_2 /Clay nanocomposites: A comparison study of different type of clays. *Journal of Alloys and Compounds*, 574-580.
- Carmen, P.J.G., Juan, A.C. and Ramon, M.T. 2017. Selective furfural Hydrogenation to furfuryl alcohol using Cu-Based catalysts supported on Clay Minerals. CrossMark.
- Chaterine, E H., and Sharpe, A. 2005. *Inorganic Chemistry*. Edition second. Pearson Education limited ISBN., 0130-39913-2.
- Cinthia, SC., Luiz CFGJ. and Jose, M A. 2014. The enhanced activity of Ca/MgAl mixed for transesterification. *Fuel Processing Technology*, 73-78.
- Ferdian, F., Syukri, and Putri. Y.E. 2019. Sintesis dan Karakterisasi Grafena Oksida dengan Support Clay Lubuk Minturun dan Uji Pendahuluan Aktivitas Katalitiknya pada Pembuatan Biodiesel Skala Laboatorium. Skripsi Jurusan Kimia:Universitas Andalas.
- Munir, M., Ahmad, M. Saeed, M. Waseem, A. Rehan, M. Nizami, A.S. Zafar, M. Arshad, M. and Sultana, S. 2019. Sustainable production of bioenergy from novel non-edible seed oil (*Prunus cerasoides*) using

- bimetallic impregnated montmorillonite clay catalyst. *Renewable and Sustainable Energy Reviews*, 109:321-332.
- Nuripati, Syukri dan Putri, Y.E. 2018. Tanah lempung limau manis: karakterisasi, modifikasi, dan uji aktivitas katalitiknya. Skripsi Jurusan Kimia FMIPA:Universitas Andalas.
- Putri, M.E., Syukri and Putri, Y.P. 2020. Lempung Terpillar CuO sebagai Katalis pada Reaksi Transesterifikasi *Crude Palm Oil* (CPO). Skripsi Jurusan Kimia:Universitas Andalas.
- Septioga, K., Syukri, and Arief, S. 2019. Kalsium Oksida dai Cangkang Telur Ayam Broiler sebagai Katalis Pada Pembuatan Biodiesel Skala Laboratorium dengan zat Pendukung Lempung Pasaman Barat. Skripsi jurusan Kimia FMIPA :Univesitas Andalas.
- Parvin, S., Rubbi, M.F. Ruman, M.A. Rahman, M.M. and Biswas, B.K. 2020. Utilization of egg-shell, a locally available biowaste material, for adsorptive removal of congo red from aqueous solution. *Aceb International Journal of Science and Technology*, 9(2).
- Suharto E. 2010. Kimia Katalis Heterogen. Jurusan Kimia Fmipa Universitas Bengkulu
- Yeslia, U., Karna, W. Triyonol. and Eko SA. 2018. Kalium Hydroxide/Zirconia Pillared Bentonite for Palm Oil Transesterification. *Oriental Journal of Chemistry*, 34(3):1484-1491.
- Yusuf, A.S., Adeniyi, O.D. Azeez, S.O. Olutoye, M.A. and Akpan, U.G 2018. Synthesis and characterization of anthill-eggshell-Ni-Co mixed oxides composite catalyst for biodiesel production from waste fring oil. *Department of chemical and petroleum Engineering*, 10:1002.
- Wahyu, S.K.N., Ahmad, S. dan Priyono. 2014. Pengaruh temperatur kalsinasi pada modifikasi clay dengan oksida aluminium sebagai pemilar. *Journal of Scientific and Applied Chemistry. Physical Chemistry Laboratory, Chemistry Department, Faculty of Sciences and Mathematics, Diponegoro University. Semarang.*, 17(2):43–47. <http://ejournal.undip.ac.id/index.php/ksa>
- Helwani, Z., Othman, MR. Aziz, N. and Fernando. WJN. 2009. Teknologi untuk produksi biodiesel dengan teknik green catalytic: review, *Fuel Proses Technol*, 90:1502-1514.