

**KAOLINITE AND ILLITE BASED CLAY SUPPORTING NICKEL:
ITS SYNTHESIS, CHARACTERIZATION,
AND CATALYTIC OPTIMAZION IN A LAB-SCALE FATTY
ACID METHYL ESTER PRODUCTION**

**F. Febiola
Rahmayeni
Admi
Syukri**

syukridarajat@sci.unand.ac.id

Universitas Andalas, Padang, West Sumatra, Indonesia

Abstract

The increasing world energy needs are not matched by the limited availability of fossil fuels thus the development of clean and sustainable fuels is the right solution. Biodiesel is one of these fuels and can be produced through transesterification reactions of vegetable oils in the presence of a catalyst. Acidic natural clay can be an option because of its large abundance, especially in the Indonesia and is heterogeneous in the solution it catalyzes. In this study, clay samples were obtained from an area in Bukittinggi City, West Sumatra Province, and then combined by wet impregnation with nickel as a catalyst in the transesterification reaction of used cooking oil to produce fatty acid methyl esters. Based on X-Ray diffraction (XRD) analysis, the presence of nickel ions does not affect the diffraction pattern of clay minerals contained in the soil consisting of kaolinite and illite. Measurements with X-Ray fluorescence (XRF) showed that the silicon-aluminum mole ratio also did not show a significant change where before mixing the value was 2.0 and after that it only decreased about 5 % to 1.9. The pore diameter of the catalyst was 3.03 nm known by Surface Area Analyzer (SAA). Several variations have been carried out to optimize the catalytic performance of the nickel supported clay and the best conditions were obtained when the catalyst concentration was 3 wt %, the methanol-oil mole ratio was 6:1, the reaction temperature

Keywords

*Biodiesel, transesterification,
WCO, clay, nickel*

was 70 °C and the reaction carried out for 3 hours. Received 30.11.2022
Under these conditions, the yield of methyl ester pro- Accepted 27.02.2023
duced was 63 % © Author(s), 2023

Syukri et al. thank the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia and LPPM of Universitas Andalas for their financial support with research contract no. 086/E5/PG.02.00.PT/2022 and T/3/UN.16.17/PT/01.03/PPS-PTMEnergi/2022

Introduction. Energy has become an important factor for mankind in continuing economic growth and maintaining a good standard of living especially after the Industrial Revolution in the late 18th century. Globally, transportation occupies the second position after the industrial sector in energy consumption, which increases ± 1.8 % per year. Unfortunately this is not comparable to the limited availability of fossil fuels [1]. In addition, pollution due to the use of fossil fuels is also a major problem facing the world today [2]. The development of clean and sustainable fuels such as biodiesel and bioethanol should thus be the best solution to overcome these problems. One of the typical biodiesel is fatty acid methyl ester which can be produced by transesterification of various types of vegetable oils [3].

Although biodiesel is a promising alternative as a substitute for diesel fuel, technological innovation and strategic policy interventions of power holders in various countries are still very much needed so that they have competitiveness with fossil diesel in the energy market. The availability of cheap and easy-to-obtain sources of triglycerides and catalysts will accelerate the development of biodiesel more broadly [4]. Fresh vegetable oils are still commonly used for biodiesel production such as those from canola, rapeseed, jatropha, sunflower, soybean, and palm oil [5]. However, this has caused a kind of controversy because of the competition for its function as a source of food. Utilization of Waste Cooking Oil (WCO) can certainly be one solution to reduce the use of fresh vegetable oil so that it also provides opportunities to prevent deforestation [6].

The transesterification reaction is influenced by several parameters, including the type of and catalyst concentration, oil and methanol molar ratio, reaction temperature and reaction time. Homogeneous base catalysts such as NaOH and KOH are not suitable for transesterification of WCO due to the high content of Free Fatty Acids (FFA) will trigger a saponification reaction which causes difficulties in separating methyl ester and glycerol. The use of homogeneous acid catalysts also poses problems, namely: corrosion of the equipment used, in addition to homogeneous catalysts which are very difficult to regenerate for reuse [4, 7].

Several problems that arise in the use of homogeneous catalysts can be overcome by converting them into heterogeneous catalysts [8, 9]. Clay is an acidic catalyst and a heterogeneous type of catalyst that shows several superior properties due to its high cation exchange capacity and relatively large specific surface area. The availability of abundant clay in nature can also reduce production costs so that it can provide an economical process [10, 11]. Previous studies have been conducted in the use of clay as both catalyst and supporting catalyst in the production of biodiesel; the clay obtained from the Indarung area of West Sumatra, which was processed by cation exchange with Ca^{2+} and Cu^{2+} ions [12] gave good methyl ester yield. Another study was clay from Lubuk Minturun, West Sumatra, combined with graphene oxide [13], which also gave promising results. Based on the literature, it is concluded that to improve the catalytic properties of clay it is necessary to modify it both physically and chemically. In other hand, acid heterogeneous catalysts such as transition metals are good to use since they are insensitive to FFA content and can catalyze esterification and transesterification reactions simultaneously, so they are widely used for biodiesel production [14].

In our previous study, it was found that the amount of biodiesel obtained from crude palm oil using Bukittinggi clay as a catalyst that had been calcined at 450 °C was twice that of uncalcined clay [15]. Nickel, which is known as a good catalyst in biomass conversion, has also previously been combined with egg shells and can even increase the yield of biodiesel up to almost 100 % [16]. These things inspired us to carry out this research with the aim of getting the maximum amount of biodiesel. The method chosen is to find the optimal conditions for clay that has been calcined at a temperature of 450 °C and has also been infiltrated with nickel ions. The optimization variables studied were catalyst concentration, methanol-oil molar ratio, temperature and reaction time.

Experimental. Material. For this study, clay was obtained from Bukittinggi (West Sumatra, Indonesia), WCO as raw material for biodiesel was collected from local fried food traders, aquadest as a solvent, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 99 % (Merck) was used as a source of nickel in the cation exchange process, and methanol 98 % (Merck) as a source of methyl groups.

Preparation of the catalyst. Nickel-modified clay was prepared by first washing the sample with distilled water, followed by centrifugation, then drying at 105 °C. Then the clay was ground and sieved (90 μm) and then labeled as h-clay (heated clay). Some of the h-clay was calcined at 450 °C for 4 hours, the sample was labeled as c-clay (calcined clay). The amount of c-clay was then

reacted with a solution of 0.5 M $\text{Ni}(\text{NO}_3)_2$ (the mass ratio of clay:volume of $\text{Ni}(\text{NO}_3)_2 = 1:7$) for 24 hours at 70 °C while stirring. The obtained catalyst rinsed with distilled water several times until the filtrate is no longer green in color. The samples were dried at 105 °C and labeled as Ni/c-clay.

Characterization of the catalyst. The composition of the parent clay elements and catalysts were analyzed with an *Epsilon 3 X-Ray Fluorescence Spectrometer* (XRF), and the mineral compositions were identified by X-Ray diffraction (XRD) using *Xpert Pro PANalytical PW30/40*. FTIR transmission spectra in the frequency range 400–4000 cm^{-1} were recorded on *Shimadzu, an IR Tracer-100 AH Spectrometer*, to analyze the presence of organic groups. Texture characterization of the catalyst samples was carried out using the gas adsorption/desorption method, at –196 °C, on a *Quantachrome Novatouch Lx4 Analyzer*. Prior to analysis, the samples were treated under vacuum at 200 °C for 3 hours. The specific surface area, S_{BET} , is calculated in the validity domain of the BET equation. Pore diameters were evaluated from nitrogen absorption isotherms, using the Broekhoff and de Boer methods.

Catalytic activity during transesterification of WCO by the Ni/c-clay catalyst. The transesterification of WCO with methanol was carried out by reflux method in a 250 mL three neck flask equipped with a condenser and thermometer. Ni/c-clay catalyst and methanol were reacted to a temperature of 50 °C while continuing to stir, then 30 mL of WCO was added. The reaction was continued with different transesterification parameters which were evaluated within the given range for Ni/c-clay catalyst concentration (1–5 wt %), methanol-oil molar ratio (6:1–18:1), reaction temperature (60–80 °C), and reaction time (2–4 hours). Optimum conditions are determined sequentially. At the end of the reaction, the flask was cooled to room temperature and the catalyst was separated from the product mixture using *Whatman No. 1* filter paper. The product is washed with hot water at a temperature of about 50 °C and then allowed to stand until a boundary is formed.

The top layer which is suspected to contain methyl ester is separated and heated until there are no more bubbles. Products suspected of containing methyl esters were analyzed qualitatively and quantitatively with GC-MS *Shimadzu QP 2010 SE* and the density was measured at 40 °C using a 5 mL pycnometer, and the mass of the resulting product was measured to determine the yield of methyl ester with the following formula [7, 8, 13]:

$$\text{Yield} = \frac{\text{Mass of methyl esters} \cdot \% \text{ FAME from GC-MS}}{\text{Mass of WCO}} \cdot 100 \%$$

Result and discussion. *Clay preparation and activation.* The preparation aims to evaporate the absorbed water, while the calcination process is to burn organic compounds and remove water that is coordinatively bound to clay minerals so as to increase the ability to exchange cations and absorb chemical compounds [17, 18]. The physical differences between h-clay and c-clay can be seen in Fig. 1, where the color changes from brown to brick red. The color change depends on the type of predominant metal oxide contained in it. The color change from brown to brick red is caused by an abundance of iron oxide in the form of hematite [19, 20]. The color change which was also followed by a change in pH from 5 to 6 indicated the release of some protons from h-clay, and also changes the pore volume from $9,2 \cdot 10^{-2}$ to $9,8 \cdot 10^{-2}$ cm³/g.



Fig. 1. Color of the clay sample before calcination (*a*) and after calcination (*b*)

Catalyst characterization. *Elemental composition.* Characterization with XRF aims to determine the composition of the elements contained in clay samples and to evaluate whether nickel can undergo cation exchange in such clay minerals. The results of the XRF characterization of clay labeled h-clay, c-clay, and Ni/c-clay can be seen in Table 1. The main composition of the Bukittinggi clay sample is Si and Al which account for almost 70 % of the total composition of all elements with a Si/Al molar ratio of h-clay is 2.0 and can be concluded that the clay sample is qualified as a clay material and has the potential to be a good catalyst [21].

Based on Table 1, 0.75 % Ni was successfully loaded into the clay followed by a decrease in the amount of all metals. Alkali and alkaline earth metals are easily replaced based on the liotropic series ($\text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+}$). However, sodium did not significantly decrease in this test, so it needs to be analyzed by XRD to see the type of mineral. Iron is the most degraded element which can be considered as a determining factor in the cation exchange process because its ionic radius (78.5 pm) is not much different from Ni^{2+} (83 pm) [22].

Table 1

**Elemental Composition of h-clay, c-clay,
and Ni/c-clay characterized by XRF**

Element	Sample		
	h-clay (%)	c-clay (%)	Ni/c-clay (%)
Si	48.50	49.40	55.74
Al	23.00	23.60	27.62
Fe	19.60	18.20	9.98
Ca	3.83	3.71	2.05
Ti	1.95	1.83	1.20
Na	1.48	1.68	1.70
K	1.25	1.21	0.61
Mg	0.34	0.37	0.35
Ni	0.00	0.00	0.75

Mineral composition. X-ray diffraction was used to characterize the types of minerals, effect of calcination, and to study cation exchange process in the clay structure. Figure 2 is the XRD diffractogram pattern of h-clay, c-clay, and Ni/c-clay. Clay minerals contain in samples were kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) according to ICDD No. 00-001-0527 and illite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$) based on ICDD No. 00-002-0050. Also another mineral like feldspar indicated by the appearance of albite peaks ($\text{Na}(\text{AlSi}_3\text{O}_8)$) based on ICDD No. 01-083-1606. The presence of albite minerals could explain why Na does not decrease after the cation exchange process.

The calcination process results in two new peaks of illite in the c-clay diffractogram at 2θ : $26,750^\circ$ and $31,589^\circ$, accompanied by weakening of several albite peaks. Albite is known as a primary mineral that is easily weathered and produces clay minerals in the form of illite [23, 24]. On the other hand, the sample showed several peaks of iron oxide in the form of goethite ($\text{FeO}(\text{OH})$) and hematite (Fe_2O_3). In addition, supports the XRF data that the color change is due to the transformation of goethite to hematite. The c-clay sample lost both goethite peaks; this is assumed to be due to the loss of H_2O after calcination of goethite to form hematite.

The enrichment process of c-clay with nickel is showed in the Ni/c-clay diffractogram; the peak shift is accompanied by a change in the basal spacing value which indicates that nickel has successfully entered the clay. The biggest change in basal spacing occurred at the main peak 27.9531° to 27.8491° which

is the peak of illite mineral with basal spacing values of c-clay and Ni/c-clay are 3.1893 and 3.2009 Å. The increase in the basal spacing value is in accordance with that reported by Asma (2017) that montmorillonite clay treated by a cation exchange process using nickel metal increases the basal distance from 1.20 to 1.71 nm [25]. After enrichment with nickel, it was found that the peaks of albite and goethite were increased again. This is thought to be due to water reentering the crystal lattice.

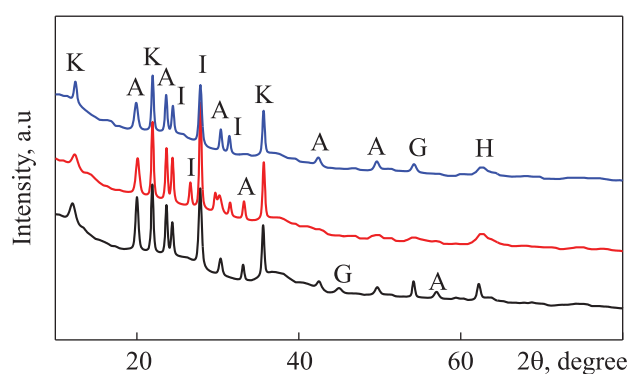


Fig. 2. XRD diffractogram of h-clay (—), c-clay (—), and Ni/c-clay (—):
K is kaolinite; I is illite; A is albite; G is goethite; H is hematite

Chemical functional groups. Characterization with FTIR aims to see the effect of calcination and the presence of Ni cations on covalent bonds in clay samples. The FTIR spectra of h-clay, c-clay, and Ni/c-clay in Fig. 3 show the same pattern but with slight changes. The absorption at 3632 cm^{-1} is the O–H stretching vibration of kaolinite, while the absorption at 1634 cm^{-1} is the H–O–H bending vibration. Both absorptions are weaker for c-clay than for h-clay, which is caused by evaporation of water after the calcination process [26].

In general, it can be seen that the c-clay absorption band has a slight shift to the left, which is towards a higher wave number. The absorption shift can be explained theoretically where there is dealumination in the clay mineral structure due to the weaker Al–O bond strength than Si–O, so that the Si–O vibration becomes more dominant and there is a shift towards a larger wave number [27]. Meanwhile, the spectrum of Ni/c-clay does not show any difference compared to c-clay, so it can be concluded that the cation exchange process does not affect the bonding of the clay.

The absorption in the fingerprint area for clay was vibration of Si–O clay minerals is around 998 cm^{-1} . Analysis of the metal present in the clay seen at the absorption of 907 cm^{-1} is the bending vibration of Fe–O–H [26].

This analysis gives an indication that the sample contains goethite compounds. At the absorption of 747 cm^{-1} , the strain vibration of Fe–OH decreases during calcination, meaning that the bond between Fe–OH is broken due to evaporation of water [28]. Then some absorptions that indicate the presence of bonds in the clay are Si–O–Al bending vibrations at 520 cm^{-1} which is a very sensitive band in the presence of Al in the octahedral layer and Si–O–Si bending vibrations at 470 cm^{-1} [27].

The Ni/c-clay spectrum that did not experience significant changes also provided information that the Ni^{2+} entering the clay was not covalently bound but only electrostatically interacted, so that Ni–OH vibrations were not detected in the FTIR spectrum of Ni/c-clay. Another important thing that was detected was the absence of a nitrate absorption band which strengthened the notion that Ni^{2+} entered the clay not in the form of nickel nitrate but in the form of the cation Ni^{2+} .

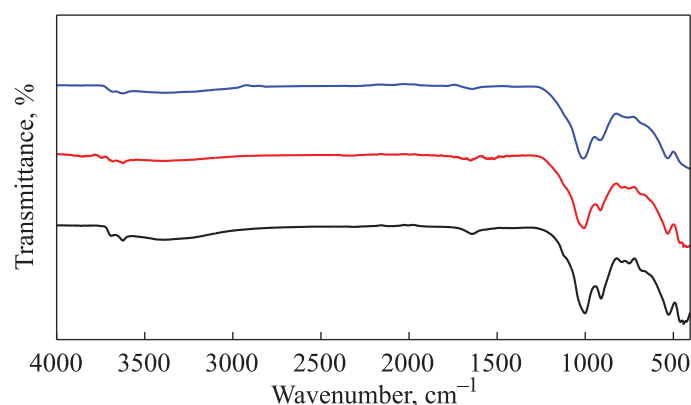


Fig. 3. FTIR spectra of h-clay (—), c-clay (—), and Ni/c-clay (—)

Textural characteristics. The N_2 adsorption-desorption isotherm at $-196\text{ }^\circ\text{C}$ from h-clay, c-clay, Ni/c-clay before reaction and Ni/c-clay after transesterification reaction samples were shown in Fig. 4. Hysteresis loop of h-clay, c-clay, and Ni/c-clay (before) can be qualified as type I and type IV intermediates with type H3 hysteresis loops exhibiting a micropore-mesopore structure. Ni/c-clay (after) isotherm with H4 type hysteresis, showing a small number of slit-like pores. Based on the adsorption data, specific surface area, total pore volume and pore diameter were measured and summarized in Table 2.

Samples of h-clay, c-clay, and Ni/c-clay (before) showed a similar surface area of about $61\text{--}64\text{ m}^2/\text{g}$. Similarities were also seen in the catalyst pore volume and pore diameter. The mesoporous diameter is about 3 nm for h-clay,

c-clay, and Ni/c-clay (before). Meanwhile, the Ni/c-clay (after) sample has a surface area of 7 m²/g which is about 9 times smaller than the Ni/c-clay (before) catalyst. A significant reduction in surface area was followed by an increase in the pore diameter. The decrease in surface area and pore volume was due to the filling of the catalyst pores by the reactants used and the resulting by-products, namely methanol, free fatty acids, and glycerol.

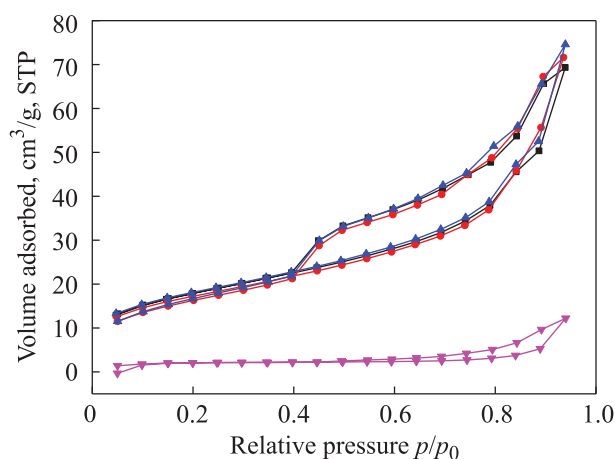


Fig. 4. N₂ adsorption-desorption isotherms at -196 °C of the h-clay (—■—), c-clay (—●—), Ni/c-clay before (—▲—) and Ni/c-clay after (—▼—) reaction samples

Table 2

Texture properties of catalysts

Sample	Surface area, m ² /g	Pore volume, cm ³ /g	Pore diameter, nm	Correlation coefficient
h-clay	63	0.092	3.39	0.99977
c-clay	61	0.098	3.03	0.99971
Ni/c-clay: before	64	0.100	3.03	0.99970
after	7	0.017	26.42	0.99242

Transesterification reaction. Effect of catalyst concentration. The experiment was carried out under the same reaction conditions (molar ratio of methanol–oil 18:1 at 70 °C for 3 hours). The effect of the catalyst has a significant effect on the yield of biodiesel produced, which can be seen below:

Catalyst concentration, %	1	3	5
Yield biodiesel, %	37.70	58.02	39.19

The low conversion when the catalyst concentration was 1 % due to the small number of active catalyst sites, thereby reducing its catalytic ability

in biodiesel conversion. Optimal conversion is obtained when the catalyst concentration is 3 % and it is assumed that under these conditions the amount of catalyst provides sufficient catalyst active sites for the reaction to reach equilibrium conditions. When the catalyst concentration is above optimal condition, the catalytic yield decreases due to the formation of a precipitate consisting of a mixture of catalyst and methanol. The mixture in the form of a slurry causes limited and not optimal catalytic activity in producing methoxide ions which function to break bonds in triglycerides [3].

Effect of methanol-WCO molar ratio. The transesterification reaction is a reversible reaction, so the use of excess methanol is also useful to drive the reaction towards the product according to Le Chatelier principle [3]. The result of the amount of FAME obtained versus the mole ratio of methanol-oil on Ni/c-clay catalyst is shown below with a 3 wt % catalyst for 3 hours at 70 °C:

Methanol-WCO molar ratio	6:1	12:1	18:1
Biodiesel yield, %	62.70	58.18	58.01

The FAME yield was found to decrease with an increase molar ratio. The maximum yield was observed to be 63 %. A decrease in the amount of biodiesel was observed after a 6:1 ratio because the by-product (glycerol) will mostly dissolve in excess methanol and then inhibit the reaction mixture between methanol, oil and catalyst. The use of excess methanol above the optimal ratio will also add new problems to the process of separating biodiesel products from residual methanol. Separation must be done because of the nature of methanol which is toxic and harmful to the environment [5, 29, 30].

Effect of the reaction temperature. Transesterification is an endothermic reaction where the temperature greatly affects the resulting product. High temperatures can help the reactants pass the activation energy so that the reaction can occur [5]. The effect of reaction temperature on the conversion of oil into biodiesel was evaluated in the range of 60 to 80 °C with the catalyst concentration and mole ratio of methanol-oil used in accordance with the results of determining the previous optimum conditions. The amount of FAME obtained in determining the optimum temperature can be seen below:

Reaction temperature, °C	60	70	80
Biodiesel yield, %	12.15	62.70	14.18

At a lower reaction temperature (60 °C) mixing between reactants did not take place optimally because the viscosity of the oil was still thick, which at higher temperatures (80 °C) the decrease in yield is thought to be due to the

reaction temperature above the boiling point of methanol, which allows evaporation of some of the alcohol. High temperatures can also cause methanol gas bubbles, which inhibit mass transfer at the interface phase and reduce the amount of biodiesel [31].

Effect of the reaction time. WCO transesterification reactions were carried out at different durations ranging from 2 hours to 4 hours to study the effect of reaction time on the amount of FAME produced [29]. The effect of reaction time on the amount of FAME shows below:

Reaction time, h	2	3	4
Biodiesel yield, %	13.29	62.70	8.27

An increase in the amount of FAME was observed in reactions with a duration of 2 and 3 hours, and a decrease in the amount of FAME at a reaction duration of 4 hours. The transesterification reaction does not occur in a short time. Over time, the feedstock (triglycerides) is converted into two main derivatives of diglycerides and monoglycerides which facilitate the production of methyl esters (biodiesel). The longer the reaction time, the more contact time between the reaction and the catalyst which causes more chance of collision. While the decrease in the amount of biodiesel after optimum time because transesterification is a reversible reaction, where the reaction will return immediately [5, 29].

Activity of catalyst. Catalyst activity in a reaction was assessed based on the amount of product produced, usually in the form of percent yield, TON, or TOF. The yield value of biodiesel produced by the Ni/c-clay catalyst with optimum reaction conditions (Ni/c-clay catalyst concentration 3 % (w/w), methanol–oil mole ratio 6:1, reaction temperature 70 °C for 3 hours) was 63 %. The yields obtained were compared with the control reaction using a homogeneous acid catalyst H₂SO₄, the c-clay catalyst that had not been enriched with nickel, and a transesterification reaction without a catalyst under the same conditions. The amount of biodiesel produced can be seen in Fig. 5.

The transesterification reaction requires a catalyst to produce a product, this is evidenced by Fig. 5. When the reaction is carried out without a catalyst there is no biodiesel in the resulting product. Meanwhile, when a homogeneous catalyst is used, namely sulfuric acid, the yield of biodiesel produced reaches 196.44 % due to transesterification and esterification reactions simultaneously, where the conversion of methyl esters does not only come from triglycerides in used cooking oil but can also come from free fatty acids. The used cooking oil is known to have a high fatty acid content. Furthermore, looking at the effect

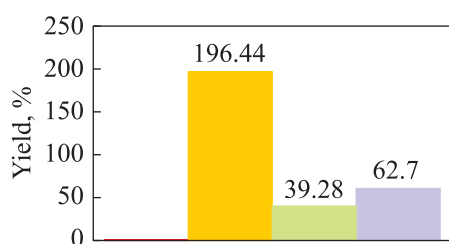


Fig. 5. Percentage of FAME yield from transesterification reaction using sulfuric acid (■), c-clay (■), Ni/c-clay (■), and without catalyst (■)

of nickel cation exchange into c-clay can increase biodiesel yield by 23.42 %. Nickel enrichment into clay succeeded in increasing the active site of the catalyst so that more FAME was produced.

Selectivity of catalyst Ni/c-clay. Catalyst selectivity is one of the important criteria in evaluating catalytic performance besides yield. The expected catalyst selectivity in the transesterification reaction in producing biodiesel is in the form of saturated methyl ester. Methyl ester saturation affects its oxidation stability, unsaturated methyl ester has lower oxidation stability. The use of methyl esters with alkyl chains containing double bonds will trigger oxidation and form acid species which will accelerate the corrosion of fuel lines and tanks [32].

Methyl ester produced in the WCO transesterification reaction using a Ni/c-clay catalyst with optimal reaction conditions (catalyst concentration of 3 wt %, methanol–oil molar ratio of 6:1, reaction temperature of 70 °C, and reaction time of 3 hours) are methyl palmitate (45 %) and methyl oleate (55 %). Based on its structure, methyl palmitate ester is a saturated methyl ester while methyl oleate ester has an unsaturated alkyl chain. The ratio of saturated and unsaturated methyl esters in the WCO transesterification reaction using a Ni/c-clay catalyst with the optimum reaction conditions is 9:11. This value indicates that the Ni/c-clay catalyst has not been selective in producing saturated methyl esters.

More unsaturated methyl esters are produced than saturated methyl esters because the innate structure of triglycerides is composed of unsaturated monoglycerides, the double bond electrons between monoglycerides in triglycerides will produce Van Der Waals repulsion forces to form spaces in triglycerides, so that Carbonyl C is more easily accessible to ions methoxide. Different things happen to triglycerides which are composed of saturated monoglycerides, there is no repulsion between electrons so that the carbonyl C access space is smaller, so the methoxide ion is more challenging to access the C carbonyl.

Conclusion. Bukittinggi clay which has been activated by calcination can contain Ni²⁺ ions as much as 0.75 wt % through a wet impregnation process at 70 °C for 24 hours. The optimum conditions for the transesterification

reaction of WCO with a thermally activated clay catalyst at 450 °C and enriched with nickel were obtained, when the nickel concentration in the catalyst was 3 wt %, the methanol–oil molar ratio was 6:1, reaction temperature was 70 °C for 3 hours with methyl ester yield of 63 %. The selectivity of the catalyst developed in this study still needs to be improved to produce more saturated FAME.

REFERENCES

- [1] Atabani A.E., Silitonga A.S., Badruddin I.A., et al. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew. Sustain. Energy Rev.*, 2012, vol. 16, iss. 4, pp. 2070–2093. DOI: <https://doi.org/10.1016/j.rser.2012.01.003>
- [2] Wei G., Liu Z., Zhang L., et al. Catalytic upgrading of Jatropha oil biodiesel by partial hydrogenation using Raney-Ni as catalyst under microwave heating. *Energy Convers. Manag.*, 2018, vol. 163, pp. 208–218. DOI: <https://doi.org/10.1016/j.enconman.2018.02.060>
- [3] Pooja S., Anbarasan B., Ponnusami V., et al. Efficient production and optimization of biodiesel from kapok (*Ceiba pentandra*) oil by lipase transesterification process: addressing positive environmental impact. *Renew. Energy*, 2021, vol. 165, part 1, pp. 619–631. DOI: <https://doi.org/10.1016/j.renene.2020.11.053>
- [4] Falowo O.A., Apanisile O.E., Aladelusi A.O., et al. Influence of nature of catalyst on biodiesel synthesis via irradiation-aided transesterification of waste cooking oil-honne seed oil blend: modeling and optimization by Taguchi design method. *Energy Convers. Manag. X*, 2021, vol. 12, art. 100119. DOI: <https://doi.org/10.1016/j.ecmx.2021.100119>
- [5] Bin Mohiddin M.N., Tan Y.H., Seow Y.X., et al. Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: a review. *J. Ind. Eng. Chem.*, 2021, vol. 98, pp. 60–81. DOI: <https://doi.org/10.1016/j.jiec.2021.03.036>
- [6] Lin Y.S., Lin H.P. Study on the spray characteristics of methyl esters from waste cooking oil at elevated temperature. *Renew. Energy*, 2010, vol. 35, iss. 9, pp. 1900–1907. DOI: <https://doi.org/10.1016/j.renene.2010.01.014>
- [7] Khan I.W., Naeem A., Farooq M., et al. Catalytic conversion of spent frying oil into biodiesel over raw and 12-tungsto-phosphoric acid modified clay. *Renew. Energy*, 2020, vol. 155, pp. 181–188. DOI: <https://doi.org/10.1016/j.renene.2020.03.123>
- [8] Abukhadra M.R., Sayed M.A. K⁺ trapped kaolinite (Kaol/K⁺) as low cost and eco-friendly basic heterogeneous catalyst in the transesterification of commercial waste cooking oil into biodiesel. *Energy Convers. Manag.*, 2018, vol. 177, pp. 468–476. DOI: <https://doi.org/10.1016/j.enconman.2018.09.083>
- [9] Alves H.J., da Rocha A.M., Monteiro M.R., et al. Treatment of clay with KF: new solid catalyst for biodiesel production. *Appl. Clay Sci.*, 2014, vol. 91–92, pp. 98–104. DOI: <https://doi.org/10.1016/j.clay.2014.02.004>

- [10] Munir M., Ahmad M., Mubashir M., et al. A practical approach for synthesis of biodiesel *via* non-edible seeds oils using trimetallic based montmorillonite nano-catalyst. *Bioresour. Technol.*, 2021, vol. 328, art. 124859.
DOI: <https://doi.org/10.1016/j.biortech.2021.124859>
- [11] Inayat A., Nassef A.M., Rezk H., et al. Fuzzy modeling and parameters optimization for the enhancement of biodiesel production from waste frying oil over montmorillonite clay K-30. *Sci. Total Environ.*, 2019, vol. 666, pp. 821–827.
DOI: <https://doi.org/10.1016/j.scitotenv.2019.02.321>
- [12] Ningsih L., Deska A., Arief S., et al. Enrichment of Sawahlunto clay with cation Ca^{2+} and Cu^{2+} and preliminary test of its catalytic activity in CPO transesterification reaction. *Aceh Int. J. Sci. Technol.*, 2020, vol. 9, no. 3, pp. 187–196.
DOI: <https://doi.org/10.13170/aijst.9.3.17944>
- [13] Syukri S., Ferdian F., Rilda Y., et al. Synthesis of graphene oxide enriched natural kaolinite clay and its application for biodiesel production. *Int. J. Renew. Energy Dev.*, 2021, vol. 10, no. 2, pp. 307–315. DOI: <https://doi.org/10.14710/ijred.2021.32915>
- [14] Lam M.K., Lee K.T., Mohamed A.R. Sulfated tin oxide as solid superacid catalyst for transesterification of waste cooking oil: an optimization study. *Appl. Catal. B Environ.*, 2009, vol. 93, iss. 1-2, pp. 134–139.
DOI: <https://doi.org/10.1016/j.apcatb.2009.09.022>
- [15] Syukri, Febiola Fifi, Rahmayeni, et al. Effect of thermal treatment and nickel-salt modification on the catalytic performance of the illite-kaolinite clay from Bukittinggi of West Sumatra in palm oil transesterification. *Herald of the Bauman Moscow State Technical University, Series Natural Sciences*, 2022, no. 2 (101), pp. 125–136.
DOI: <https://doi.org/10.18698/1812-3368-2022-2-125-136>
- [16] Kamarozaman M.F.F., Kahar H., Hassan N., et al. Biodiesel production from waste cooking oil using nickel doped onto eggshell catalyst. *Mater. Today Proc.*, 2020, vol. 31, part 1, pp. 342–346. DOI: <https://doi.org/10.1016/j.matpr.2020.06.159>
- [17] Gonggo S.T., Edyanti F. Physicochemical characterization of clay minerals as a raw material of ceramic industry in Desa Lembah Bomban Kec. *Bolano Lambunu Kab. Parigi Moutong, Akad. Kim.*, 2013, vol. 2, no. 2, pp. 105–113.
- [18] Suyanto T., Kismolo E. Karakterisasi Kapasitas Tukar Kation Lempung Kasongan untuk Pengolahan Limbah Radioaktif Cair. *Penelitian dan Pengelolaan Preengkat Nuklir*, 2008, pp. 236–240.
- [19] Handayani S. Kualitas Batu Bata Merah Dengan Penambahan Serbuk Gergaji. *J. Tek. Sipil dan Perenc.*, 2010, vol. 12, no. 1, pp. 41–50.
DOI: <https://doi.org/10.15294/jtsp.v12i1.1339>
- [20] Alaa S., Kurniawidi D.W. Pengaruh Suhu Pemanasan Lempung terhadap Sifat Mekanis Gerabah. *Kuanta*, 2015, vol. 1, no. 1, pp. 32–35.
- [21] Utami D.N. Kajian Jenis Mineralogi Lempung Dan Implikasinya Dengan Gerakan Tanah. *J. Alami J. Teknol. Reduksi Risiko Bencana.*, 2018, vol. 2, no. 2, p. 89.

- [22] Bijang C.M., Sekewael S.J., Koritelu J.A. Aktivasi Lempung dengan Basa dan Aplikasinya sebagai Penukar Kation untuk Mengurangi Konsentrasi Ion Mg^{2+} dan Ca^{2+} dalam Air Sumur. *Ind. J. Chem. Res.*, 2014, vol. 1, pp. 93–98.
- [23] Rahmaniah R., Reskywijaya R., Wahyuni A.S., et al. Analisis Mineral Tanah Rawan Longsor Menggunakan X-Ray Diffraction Di Desa Sawaru Kabupaten Maros. *Jambura Geosci. Rev.*, 2020, vol. 2, no. 1, pp. 41–49.
DOI: <https://doi.org/10.34312/jgeosrev.v2i1.2639>
- [24] Noer Aini L., Mulyono M., Hanudin E. Mineral Mudah Lapuk Material Piroklastik Merapi dan Potensi Keharaannya Bagi Tanaman. *Planta Trop. J. Agro Sci.*, 2016, vol. 4, no. 2, pp. 84–94. DOI: <https://doi.org/10.18196/pt.2016.060.84-94>
- [25] Aid A., Andrei R.D., Amokrane S., et al. Ni-exchanged cationic clays as novel heterogeneous catalysts for selective ethylene oligomerization. *Appl. Clay Sci.*, 2017, vol. 146, pp. 432–438. DOI: <https://doi.org/10.1016/j.clay.2017.06.034>
- [26] Ritonga P.S. Kajian Spektra IR dan AAS Lempung Terpillar-Fe. *Phot. J. Sain dan Kesehat.*, 2012, vol. 3, no. 1, pp. 37–44. DOI: <https://doi.org/10.37859/jp.v3i1.147>
- [27] Karelius K. Extraction and characterization natural clay of central Kalimantan as one of alternatives additives of geopolymer concrete. *Balanga*, 2017, vol. 5, no. 2, pp. 1–10.
- [28] Zviagina B.B., Drits V.A., Dorzhieva O.V. Distinguishing features and identification criteria for K-dioctahedral 1 M micas (illite-aluminoceladonite and illite-glaucosite-celadonite series) from middle-infrared spectroscopy data. *Minerals*, 2020, vol. 10, iss. 2, art. 153. DOI: <https://doi.org/10.3390/min10020153>
- [29] Olutoye M.A., Wong S.W., Chin L.H., et al. Synthesis of fatty acid methyl esters via the transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst. *Renew. Energy*, 2016, vol. 86, pp. 392–398.
DOI: <https://doi.org/10.1016/j.renene.2015.08.016>
- [30] Zaki M., Husin H., M.T., et al. Transesterifikasi Minyak Biji Buta-Buta menjadi Biodiesel pada Katalis Heterogen Kalsium Oksida (CaO). *J. Rekayasa Kim. Lingkungan*, 2019, vol. 14, no. 1, pp. 36–43. DOI: <https://doi.org/10.23955/rkl.v14i1.13495>
- [31] Zabeti M., Wan Daud W.M.A., Aroua M.K. Activity of solid catalysts for biodiesel production: a review. *Fuel Process. Technol.*, 2009, vol. 90, iss. 6, pp. 770–777.
DOI: <https://doi.org/10.1016/j.fuproc.2009.03.010>
- [32] Ridho M.R., Wirawan I.K.G., Ghurri A. Pengaruh Variasi Temperatur dan Putaran Pada Proses Partial Hydrogenation Biodiesel Minyak Jelantah Terhadap Stabilitas Oksidasi. *J. Ilm. Tek. Desain Mek.*, 2020, vol. 9, pp. 3–8.

Febiola Fifi — M. Sc., Coworker, Chemistry Department, Universitas Andalas (Kampus UNAND Limau Manis, Padang, West Sumatra, Indonesia).

Rahmayeni — Dr., Professor, Lecturer, Chemistry Department, Universitas Andalas (Kampus UNAND Limau Manis, Padang, West Sumatra, Indonesia).

Admi — M. Sc., Lecturer, Chemistry Department, Universitas Andalas (Kampus UNAND Limau Manis, Padang, West Sumatra, Indonesia).

Syukri — Dr., Lecturer, Chemistry Department, Universitas Andalas (Kampus UNAND Limau Manis, Padang, West Sumatra, Indonesia).

Please cite this article as:

Febiola F., Rahmayeni, Admi, et al. Kaolinite and illite based clay supporting nickel: its synthesis, characterization, and catalytic optimization in a lab-scale fatty acid methyl ester production. *Herald of the Bauman Moscow State Technical University, Series Natural Sciences*, 2023, no. 4 (109), pp. 159–174.

DOI: <https://doi.org/10.18698/1812-3368-2023-4-159-174>