

CLAY ENRICHED WITH Ca^{2+} AND Cu^{2+} AS THE CATALYST FOR THE PRODUCTION OF METHYL ESTERS FROM CPO ON A LABORATORY SCALE

Aju Deska¹, Zulhadjri¹, Olly Norita Tetra², Mai Efdi³, Syukri¹, ✉

<https://doi.org/10.23939/chcht16.04.678>

Abstract.¹ Indarung clay (Padang city, Indonesia) has been successfully enriched with Ca^{2+} and Cu^{2+} ions. XRF, XRD, FTIR, and SAA analyses confirmed that calcination process had no significant effect on improving its performance so that the clay was simply heated at 383 K before use. Measurements using AAS showed that the clay is enriched with Cu^{2+} ions more easily than Ca^{2+} ions. The catalytic activity test carried out for the transesterification of crude palm oil showed that under the same reaction conditions Cu^{2+} enriched Indarung clay yields most methyl ester to compare with other four catalysts (Ca^{2+} enriched clay, parent clay, Ca-nitrate and Cu-nitrate).

Keywords: clay, transesterification, crude palm oil, methyl ester, heterogeneous catalyst.

1. Introduction

Currently we are faced with the problem of unstable crude palm oil (CPO) prices, and Indonesia, which is known as one of the largest CPO producers in the world, is also affected by this problem. In order to increase the economic value of CPO, the process of converting this material into a methyl ester, which can be used as biodiesel, is considered to be able to help solve the above problems while providing solutions to the world's increasing energy needs.¹ Chemically, the conversion of triglyceride-containing CPO, a polyester, to a monoester form known as methyl ester requires a catalyst. Up to now the most widely used catalyst is a typical homogeneous catalyst, namely the base from alkaline and alkaline earth. The problem that always arises in the use of homogeneous

catalysts is the difficulty in purifying the methyl ester product.² Therefore, the use of heterogeneous catalysts is a necessity, because it provides easy separation of products and can be used repeatedly. Among many heterogeneous catalysts, the use of inorganic natural materials such as clay, zeolite and bentonite are attractive because of their very low price and availability. The combination of those natural inorganic substances with the alkaline catalysts has been widely used. A number of researchers have conducted experiments to determine the activity of alkaline, alkaline earth, and transition metals supported by natural inorganic minerals, especially to catalyze organic reactions. Some of them are calcium-montmorillonite,³ sodium hydroxide-kaolinite,⁴ potassium hydroxide-kaolinite with cobalt and co-catalyst Et_3NHSO_4 ,⁵ barium-montmorillonite,⁶ calcium-MgAl,⁷ potassium hydroxide-bentonite,⁸ sodium-bentonite,⁹ palladium pillared montmorillonite,¹⁰ cadmium-mangan-montmorillonite,¹¹ and other applications in the use of magnesium oxide (MgO)-supported Al metal for the synthesis of chalcones with the aim of enlarging pores and increasing its catalytic activity.¹²

In this work the idea is how to enrich natural inorganic compounds with more active catalytic site, namely metal ions so that the catalytic ability can be improved. Among the natural inorganic compounds described above, clay is found to be more environmentally friendly, easier to obtain, and also relatively cheaper. Based on all the explanations above, in this article we present the use of a clay obtained from Indarung region of Padang city, (Indonesia), which then was enriched with Ca^{2+} and Cu^{2+} ions separately to catalyze the conversion of CPO to methyl ester.

2. Experimental

2.1. Materials

Natural clay was obtained from Indarung, a suburb of Padang city, West Sumatera Province, Indonesia Republic. The sources of Ca^{2+} and Cu^{2+} ions for clay enrichment are calcium(II) nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)

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

² Laboratory of Physical Chemistry, University of Andalas, Padang, Indonesia

³ Laboratory of Natural Product Chemistry, University of Andalas, Padang, Indonesia

✉ syukridarajat@sci.unand.ac.id

© Deska A., Zulhadjri, Tetra O.N., Efdi M., Syukri, 2022

and copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) purchased from Merck. The raw materials for producing methyl esters are crude palm oil (CPO, obtained from one of the oil-producing company) and methanol, purchased from Merck.

2.2. Methods

2.2.1. Clay preparation

Indarung clay samples were heated at 383 K for 4 h. After cooling, the samples were crushed and filtered with a 180 µm sieve to obtain a powder. The filtered clay powder was furtherly coded as h-clay (heated-clay) and then characterized by XRF, XRD, FTIR, and SAA.

2.2.2. Clay calcination

The h-clay sample was washed with distilled water and centrifuged for 15 min at the stirring speed of 3000 rpm, then dried at 383 K for 2 h. After cooling, it was heated again at 423 K for 2 h. Then 100 g of the sample was calcined at 973 K for 8 h. After being cooled again, it was crushed and filtered with 180 µm filter paper. The samples were labeled as c/h-clay (calcined h-clay) and characterized using XRF, XRD, FTIR, and SAA.

2.2.3. Clay enrichment

Prior to the enrichment process, a h-clay sample was prepared by washing with distilled water and drying at 383 K. It was then crushed and filtered with a 180 µm sieve. 20 g of the clay powder was mixed with 200 mL of 0.26M calcium nitrate and stirred at 500 rpm for 24 h at room temperature. The next 20 g of the h-clay were also prepared with the same procedure but with the reaction being run at a higher temperature, *i.e.* 343 K. The solids were separated through filtering, then were heated at 383 K for 2 h. Ca²⁺-enriched clays prepared at room temperature and 343 K were labeled as Ca/h-clay^{RT} and Ca/h-clay⁷⁰, respectively. The same procedure was carried out for the enrichment of h-clay with Cu²⁺ ions with similar volume and concentration, which were labelled as Cu/h-clay^{RT} and Cu/h-clay⁷⁰. The filtrate resulted from the screening was analyzed using AAS and all solid samples were dried and then characterized using XRD.

2.2.4. Transesterification of CPO

A set of equipment consisting of a 500 mL three-neck flask connected with a reflux condenser and equipped with a thermometer was mounted on a hot magnetic stirrer. The reaction conditions were made constant for all types of catalysts tested with the oil/methanol mole ratio of 1:6, the catalyst/methanol mole ratio of 1:10, and reaction temperature of 338 K. All reactions were carried out under 750 rpm stirring for 4 h. Firstly, the catalyst and

methanol were heated to 323 K under continuous stirring. Subsequently, 60 mL of CPO was added to the three-neck flask, which had previously been heated at 373 K until no more water bubbles remained. After allowing the temperature drop to 323 K, the catalyst, methanol, and CPO were mixed. For all catalytic examination, the transesterification reaction was carried out for 4 h at 338 K with the stirring speed of 750 rpm. At the end of the reaction, the flask was allowed to cool to room temperature and the catalyst was separated from the product mixture by filtration. Biodiesel products are separated from glycerol using separating funnels followed by washing with hot distilled water (323 K) with the water : biodiesel ratio of 1:1 (v/v). It was then followed by shaking for 5 min to form a white liquid. The mixture was allowed to stand so the water collected at the bottom and the desired methyl ester was in the upper layer. The upper layer was released from the remaining water by heating to a temperature above the boiling point of water (383 K) until there were no more water bubbles. The amount of methyl ester product obtained in the form of yield is formulated as:

$$Yield (\%) = \frac{\text{Top layer product} \times \% \text{ FAME of top layer product}}{\text{CPO mass used}} \times 100 \% \quad (1)$$

3. Results and Discussion

3.1. Effect of Calcination

3.1.1. Elemental analysis

Based on elemental analysis using XRF (Table 1), it can be explained that the main compositions of Indarung clay are Si, Al, and Fe. The calcination of the Indarung h-clay sample labeled as c/h-clay at 973 K caused only slight change in the composition represented by the Si/Al mole ratio. The process underwent an insignificant change, namely only 1 % from 2.58 to 2.55. However, this indicates that Indarung clay was very thermally stable in terms of its chemical composition resistance. From the same analysis, it can be seen that the clay samples are dominated by silica and alumina which are always found in all types of natural clays.¹³ The Ca content in h-clay was found to be almost one hundred times higher than the Cu content, which indicates that the clay has potential both as a catalyst and as a cation exchange.

3.1.2. Crystal analysis

XRD patterns of the h-clay and c/h-clay samples are depicted in Fig. 1. Referring to the International Center for Diffraction Data (ICDD) standards, Indarung clay has been shown to contain two types of minerals that

characteristic for most clays. The sample is kaolinite appearing at the angle of 20° and illite at the angle of 60° . Other types of determined minerals are quartz, which is the most dominant mineral and occurs at the angle of 27° , hematite at 41° , and bentonite at 54° .¹⁴⁻¹⁷ The c/h-clay diffractogram in Fig. 1b shows that the calcination process at very high temperatures in general does not affect the crystallinity pattern of the clay sample, where the h-clay and c/h-clay diffraction patterns were found to be quite identical with a slight difference.

3.1.3. Chemical bonding analysis

Fig. 2 shows the appearance of the Si–O stretching vibration at 663 cm^{-1} and the Si–O–Si bending vibration at 780 cm^{-1} for both h-clay and c/h-clay types. The comparative broadband between $700\text{--}900\text{ cm}^{-1}$ for h-clay and c/h-clay indicates the presence of edge oxygen sharing of the AlO_4 group from the kaolinite group.¹⁹ It was found that the vibrations of organic functional groups such as the C=C bond appeared at 1049 cm^{-1} and the C–H – at 1369 cm^{-1} . After changing to c/h-clay, the organic absorption bands disappear.²⁰

3.1.4. Specific surface area analysis (SAA)

Measurement of the specific surface area of h-clay and c/h-clay with SAA equipment using BET calculations showed interesting results – the h-clay original surface area of $42.3\text{ m}^2/\text{g}$ decreased to $20.4\text{ m}^2/\text{g}$ after calcined at the temperature of 973 K . This phenomenon can be explained by the fact that both clay samples are typical isotherm II with a layered structure and after calcination there is an increase in the number of layers resulting in a decrease in the specific surface area.²¹ So, based on the results of measurements with XRF, XRD, FTIR, and SAA both for h-clay and c/h-clay, we decided to use only the h-clay for the next process.

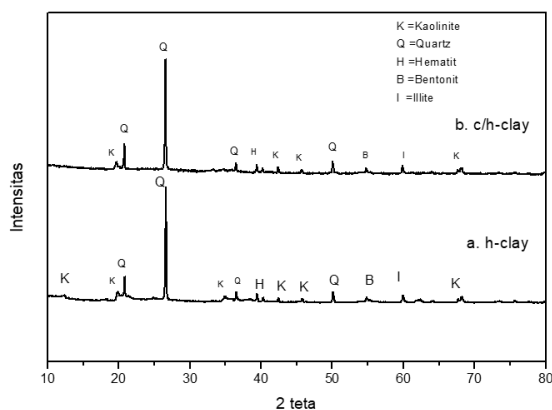


Fig. 1. XRD pattern of h-clay (a) and c/h-clay (b)

3.2. Enrichment of h-Clay

3.2.1. Loading capacity of h-clay to Ca^{2+} and Cu^{2+}

Based on the measurement of Ca and Cu levels with AAS, the enrichment process of Indarung clay with Cu^{2+} cations is easier than with Ca^{2+} cations (Table 2). Theoretically it can be explained by the difference in the ion radius sizes; Cu^{2+} ion size is relatively smaller, it is around three-quarters of the of the calcium ion size.²² It is predicted that Cu^{2+} ions can more easily penetrate the pores of the clay framework, namely between the aluminate and the silicate sheets. The next finding was that the process of Indarung clay enrichment with these two ions occurred more easily at room temperature than at higher temperatures (343 K). As explained in the previous section, when clay is treated at higher temperatures, it tends to form more layers making it more difficult for ions to access the negative sites between these layers.²²

3.2.2. Crystal analysis

In the application of clay as a catalyst and catalyst support, there is a very important factor, namely the stability of the crystal structure both against high temperatures and to the entry and exit of the catalytically active central metal cations. We discussed the thermal stability of Indarung clay as written above, in this section we show the chemical resistance of Indarung clay after being enriched with Ca^{2+} and Cu^{2+} cations separately. It can be concluded (cf. Figs. 1b, 1c and Fig. 3a) that the enrichment process can be achieved without affecting the crystallinity of the parent clay making two materials (Ca/h-clay and Cu/h-clay) as good candidates for heterogeneous catalysts.

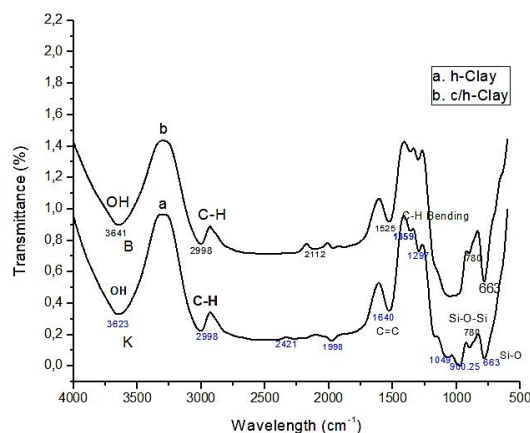


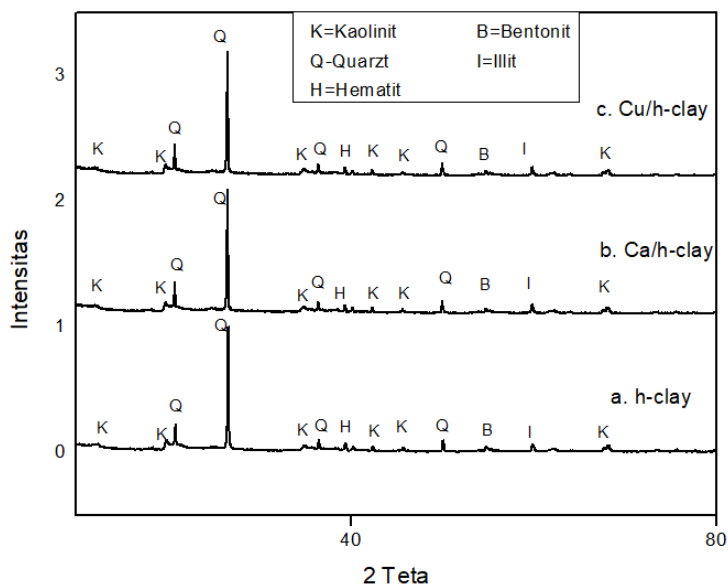
Fig. 2. FTIR spectra of h-clay (a) and c/h-clay (b)

Table 1. Comparison of elemental composition between h-clay and c/h-clay

Sample	Elements, %										
	Si	Al	Fe	K	P	Ca	Ti	Mg	Ag	Eu	Cu
h-clay	59.80	22.40	10.70	2.80	1.00	0.95	0.90	0.50	0.60	0.06	0.01
c/h-clay	57.67	21.80	12.00	3.00	0.00	1.00	1.10	2.20	0.90	0.06	0.01

Table 2. The capacity of h-clay to be enriched with Ca²⁺ and Cu²⁺ at two different temperature

Metal	Sample	Loading capacity ions metals (% w/w)	
		Room temperature	Temperature 343 K
Ca ²⁺	Ca/h-clay	5.36	2.43
Cu ²⁺	Cu/h-clay	10.96	5.84

**Fig. 3.** XRD pattern of h-clay (a), Ca/h-clay (b) and Cu/h-clay (c)

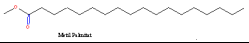
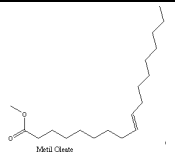
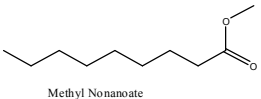
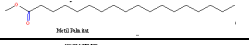
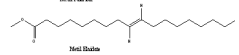

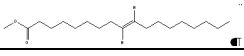
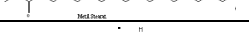
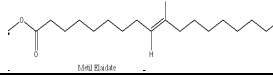
3.2.2. Test for catalytic activity

The catalytic test for the transesterification reaction of CPO to obtain methyl ester was carried out for all catalysts prepared, which are h-clay, Ca/h-clay, and Cu/h-clay with two other catalysts (Ca-nitrate and Cu-nitrate), as a comparison (Table 3). For all catalytic reactions carried out, the reaction conditions are specified as following: CPO/crystal methanol molar ratio 1:6, catalyst/methanol ratio 1:10, temperature 338 K, reaction time 4 h, the stirring speed 750 rpm. The mixing of the catalyst with methanol is done first to facilitate the formation of methoxide anions, which will attack the carbonyl triglycerides so that they are simplified into a monoglyceride form. The methyl ester product was calculated based on Eq.(1) in the GC/MS baseline data. Based on the results shown in Table 3, it can be explained that the enrichment process of Indarung clay with Cu²⁺

gives the best results when compared to Ca-nitrate and h-clay, which was then assumed that the presence of Cu²⁺ ions also increases the catalytic activity of h-Clay in producing FAME, from 31 to 56 % (almost twice).

Although the increase in catalytic activity is not as good as Cu/h-clay, Ca/h-clay still shows better catalytic activity than Ca-nitrate and h-clay. Theoretically, it can be explained that clay has layers and pores with a large enough surface area, besides acting as a catalyst, it also helps the process of distributing Cu²⁺ and Ca²⁺ ions evenly to increase the number of catalytic active sites. In this study, the Ca-nitrate catalyst gave the most selective product, namely FAME with saturated alkyl chains, while other four catalysts gave both FAME with saturated and unsaturated chains. For further research, we will focus our efforts on producing clay-based catalysts that can direct the FAME product to its mostly saturated form so as to meet the required biodiesel standards.²³

Table 3. The results of activity and selectivity of several catalysts tested in this study

Catalyst	Yield, %	Methyl ester	Molecular formula	Molecular structure	Saturated:unsaturated methyl esters
Cu-nitrate	48	Palmitic acidmethyl ester	C ₁₇ H ₃₄ O ₂		51 : 49
		Oleic acid methyl ester	C ₁₉ H ₃₆ O ₂		
Ca-nitrate	31	Nonanoic acid methyl ester	C ₁₀ H ₂₀ O ₂		100
Ca/h-clay	45	Palmitic acid methyl ester	C ₁₇ H ₃₄ O ₂		49 : 51
		Elaidic acid methyl ester	C ₁₉ H ₃₆ O ₂		
Cu/h-clay	56	Stearic acid methyl ester	C ₁₉ H ₃₈ O ₂		45 : 55
		Elaidic acid methyl ester	C ₁₉ H ₃₆ O ₂		
h-clay	31	Palmitic acid methyl ester	C ₁₇ H ₃₄ O ₂		40 : 60
		Elaidic acidmethyl ester	C ₁₉ H ₃₆ O ₂		

4. Conclusions

Based on XRF and XRD analysis it can be concluded that the main elements of Indarung clay are Si, Al, and Fe with a Si/Al molar ratio of 2.6; it consists of kaolinite, illite, and bentonite as distinctive clay minerals along with quartz and hematite. Furthermore, the results of XRF, XRD, FTIR, and SAA analysis of the clay before and after calcination show that Indarung clay does not require heating at a high temperature and it is enough to heat it to 383 K to remove moisture before being used as a catalyst or catalyst support for Ca²⁺ and Cu²⁺. Based on measurements of Ca and Cu levels by AAS it was found that the enriching of clay with Ca²⁺ and Cu²⁺ ions is sufficient to be carried out at room temperature without the need for heating at higher temperatures. It was also found that clay absorbs Cu more easily than Ca ions. All the catalysts tested under the same reaction conditions were shown to be catalytically active to produce methyl esters from CPO wherein Cu enriched clays gave the best results under the same reaction conditions. In terms of selectivity, all the catalysts tested proved to produce two types of methyl esters: saturated and unsaturated, except for Ca-nitrate, which produces only saturated chain methyl ester compounds.

Nomenclature

h-clay – heated clay

c/h-clay – calcinated/heated clay

h – hour

XRD – X-ray diffraction

FTIR – Fourier transform infrared

AAS – atomic absorption spectroscopy

SAA – surface area analysis

GC-MS – gas chromatography-mass spectroscopy

CPO – crude palm oil

FAME – fatty acid methyl ester

XRF – X-ray fluorescence

Acknowledgments

We would like to thank the Faculty of Mathematics and Natural Sciences, Andalas University for supporting this research financially through the 2019 Fiscal Year Research Grants with contract number 20 / UN.10.03.D / PP / FMIPA / 2019.

References

- [1] Jiménez-Gómez, C.P.; Cecilia, J.A.; Moreno-Tost, R.; Maireles-Torres, P. Selective Furfural Hydrogenation to Furfuryl Alcohol using Cu-based Catalysts Supported on Clay Minerals. *Top. Catal.* 2017, 4. <https://doi.org/10.1007/s11244-017-0804-2>. (accessed Aug 20, 2020)
- [2] Leung, D.Y.C; Wu, X.; Leung, M.K.H. A Review on Biodiesel Production Using Catalyzed Transesterification. *Appl. Energy* 2010, 87, 1083–1095. <https://doi.org/10.1016/j.apenergy.2009.10.006>
- [3] Jia, L.; Li, Y.; Chen, J.; Guo, X.; Lou, S.; Duan, H. Montmorillonite-Supported KF/CaO: A New Solid Base Catalyst

- for Biodiesel Production. *Res. Chem. Intermed.* **2016**, *42*, 1791–1807. <https://doi.org/10.1007/s11164-015-2118-y>
- [4] Dang, H.T.; Chen, B.-H.; Lee, D.-J. Optimization of Biodiesel Production from Transesterification of Triolein Using Zeolite LTA Catalysts Synthesized from Kaolin Clay. *J. Taiwan Inst. Chem. Eng.* **2017**, *79*, 14–22. <https://doi.org/10.1016/j.jtice.2017.03.009>
- [5] Man, Z.; Elsheikh, Y.A.; Bustam, M.A.; Yusup, S.; Mutalib, M.I.A.; Muhammad, N. A Bronsted Ammonium Ionic Liquid-KOH Two-Stage Catalyst for Biodiesel Synthesis from Crude Palm Oil. *Ind. Crops Prod.* **2012**, *41*, 144–149. <https://doi.org/10.1016/j.indcrop.2012.04.032>
- [6] Olutoye, M.A.; Wong, S.W.; Chin, L.H.; Amani, H.; Asif, M.; Hameed, B.H. Synthesis of Fatty Acid Methyl Esters via the Transesterification of Waste Cooking Oil by Methanol with a Barium-Modified Montmorillonite K10 Catalyst. *Renew. Energy* **2015**, *86*, 392–398. <https://doi.org/10.1016/j.renene.2015.08.016>
- [7] Castro, C.S.; Garcia Jr., L.C.F.; Assaf, J.M. The Enhanced Activity of Ca/MgAl Mixed Oxide for Transesterification. *Fuel Process. Technol.* **2014**, *125*, 73–78. <https://doi.org/10.1016/j.fuproc.2014.03.024>
- [8] Soetaredjo, F.E.; Ayucitra, A.; Ismadji, S.; Maukar, A.L. KOH/Bentonite Catalysts for Transesterification of Palm Oil to Biodiesel. *Appl. Clay Sci.* **2011**, *53*, 341–346. <https://doi.org/10.1016/j.clay.2010.12.018>
- [9] Abukhadra, M.R.; Ibrahim, S.M.; Yakout, S.M.; El-Zaidy, M.E.; Abdeltawab, A.A. Synthesis of Na⁺ Trapped Bentonite/Zeolite-P Composite as a Novel Catalyst for Effective Production of Biodiesel from Palm Oil; Effect of Ultrasonic Irradiation and Mechanism. *Energy Convers. Manag.* **2019**, *196*, 739–750. <https://doi.org/10.1016/j.enconman.2019.06.027>
- [10] Vellayan, K.; González, B.; Trujillano, R.; Vicente, M.A.; Gil, A. Pd Supported on Cu-Doped Ti-Pillared Montmorillonite as Catalyst for the Ullmann Coupling Reaction. *Appl. Clay Sci.* **2018**, *160*, 126–131. <https://doi.org/10.1016/j.clay.2017.12.037>
- [11] Munir, M.; Ahmad, M.; Saeed, M.; Waseem, A.; Rehan, M.; Nizami, A.-S.; Zafar, M.; Arshad, M.; Sultana, S. Sustainable Production of Bioenergy from Novel Non-Edible Seed Oil (Prunus cerasoides) Using Bimetallic Impregnated Montmorillonite Clay Catalyst. *Renew. Sust. Energ. Rev.* **2019**, *109*, 321–332. <https://doi.org/10.1016/j.rser.2019.04.029>
- [12] Katkar, S.S.; Katgaonkar, A.H.; Vidhate K.N. MgO Supported Al₂O₃ Oxide: A New, Efficient, and Reusable Catalyst for Synthesis of Chalcones. *Chem. Chem. Technol.* **2020**, *14* (2), 169–176. <https://doi.org/10.23939/chcht14.02.169>
- [13] Nugroho, W. S. K.; Suseno, A.; Priyono, P. Pengaruh Temperatur Kalsinasi pada Modifikasi Lempung dengan Oksida Aluminium sebagai Pemilar. *Jurnal Kimia Sains dan Aplikasi* **2014**, *17* (2), 43–47. <https://doi.org/10.14710/jksa.17.2.43-47>
- [14] McMurdie, H.F.; Morris, M.C.; Evans, E.H.; Paretzkin, B.; Wong-Ng, W.; Ettliger, L.; Hubbard, C.R. Standard X-Ray Diffraction Powder Patterns from the JCPDS Research Associateship. *Powder Diffr.* **1986**, *1* (2), 64–77. <https://doi.org/10.1017/S0885715600011593>
- [15] Antic, B.; Kremenovic, A.; Nikolic, A.S.; Stoilkovic, M. Cation Distribution and Size-Strain Microstructure Analysis in Ultrafine Zn–Mn Ferrites Obtained from Acetylacetonato Complexes. *J. Phys. Chem. B* **2004**, *108*, 12646–12651. <https://doi.org/10.1021/jp036214v>
- [16] Tsipurski, S.I.; Drits, V.A. The Distribution of Octahedral Cations in the 2:1 Layers of Dioctahedral Smectites Studied by Oblique-Texture Electron Diffraction. *Clay Miner.* **1984**, *19*, 177–193. <https://doi.org/10.1180/claymin.1984.019.2.05>
- [17] Drits, V.A.; Zviagina, B.B.; McCarty, D.K., Salyn, A.L. Factors Responsible for Crystal-Chemical Variations in the Solid Solutions from Illite to Aluminoceladonite and from Glauconite to Celadonite. *Am. Mineral.* **2010**, *95* (2-3), 348–361. <https://doi.org/10.2138/am.2010.3300>
- [18] Neder, R.B.; Burghammer, M.; Grasl, Th.; Schulz, H.; Bram, A.; Fiedler, S. Refinement of the Kaolinite Structure from Single-Crystal Synchrotron Data. *Clays Clay Miner.* **1999**, *47*, 487–494. <https://doi.org/10.1346/CCMN.1999.0470411>
- [19] Chakraborty, A.K. *Phase Transformation of Kaolinite Clay* [Online]; Springer Nature, 2014. <https://link.springer.com/book/10.1007%2F978-81-322-1154-9> (accessed July 17, 2020).
- [20] Djomgoue, P.; Njopwouo, D. FT-IR Spectroscopy Applied for Surface Clays Characterization. *J. Surf. Mater. Adv. Technol.* **2013**, *3* (4), 275–282. <https://doi.org/10.4236/jsemat.2013.34037>
- [21] Naderi, M. Chapter Fourteen - Surface Area: Brunauer–Emmett–Teller (BET). In *Progress in Filtration and Separation*; Tarleton, S., Eds.; Academic Press: UK, 2015; pp 586–608. <https://doi.org/10.1016/b978-0-12-384746-1.00014-8>
- [22] Housecroft, C.; Sharpe, A.J. *Inorganic Chemistry*, 2nd edn.; Pearson: London, 2005.
- [23] Puhan, S.; Saravanan, N.; Nagarajan, G.; Vedaraman, N. Effect of Biodiesel Unsaturated Fatty Acid on Combustion Characteristics of a DI Compression Ignition Engine. *Biomass Bioenergy* **2010**, *34*, 1079–1088. <https://doi.org/10.1016/j.biombioe.2010.02.017>

Received: October 26, 2020 / Revised: November 19, 2020 / Accepted: February 08, 2021

ЗБАГАЧЕНА Са²⁺ і Cu²⁺ ГЛИНА ЯК КАТАЛІЗАТОР ДЛЯ ОДЕРЖАННЯ МЕТИЛОВИХ ЕСТЕРІВ З СИРОЇ ПАЛЬМОВОЇ ОЛІЇ В ЛАБОРАТОРНИХ МАСШТАБАХ

Анотація. Проведено збагачення глини (Індарунг, Індонезія) йонами Са²⁺ і Си²⁺. За допомогою аналізів XRF, XRD, FTIR та SAA підтверджено, що процес прожарювання не має значного впливу на покращення характеристик, тому перед використанням глину просто нагрівали до 383 К. Результати ААС показали, що глина легше збагачується Си²⁺, ніж йонами Са²⁺. Встановлено, що при переестерифікації сирової пальмової олії, проведеної за однакових умов, найвищий вихід метилового естеру досягається при використанні як каталізатора глини, збагаченої Си²⁺, порівняно з іншими чотирма каталізаторами (глина, збагачена Са²⁺, сира глина, нітрат кальцію та Си-нітрат).

Ключові слова: глина, переестерифікація, сира пальмова олія, метиловий естер, гетерогенний каталізатор.

