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Separation of Kaolinite from Clay Minerals and Its Catalytic Activity in Transesterification Reactions

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Abstract

Kaolinite is a type of clay mineral that has the potential to be used as a heterogeneous catalyst in transesterification reactions. However, natural clay still contains a mixture of minerals that occur together. Therefore, as an effort to search for cheaper catalysts to reduce the price of biodiesel production, this study carried out the separation of kaolinite from natural clay and tested its performance as a catalyst in biodiesel production from Waste Cooking Oil (WCO). Separation of the kaolinite fraction was carried out with the help of NH_4Cl as a dispersing agent. The main mineral composition of clay as quartz, kaolinite, montmorillonite and hematite. After the separation process, the crystallinity of the minerals experienced an increase marked by an increase in the intensity of several kaolinite peaks, namely in the 2θ 12.24° area from 103 to 108 and at 25.00° from 95 to 125. Thermal modification caused the loss of several kaolinite peaks in the area. 2θ 12.17°; 24.94° and 62.39°. The Si/Al ratio decreased after the fractionation and calcination processes. Average particle size of h-clay decreased from 27.61 µm to 21.09 µm in K-clay. The K-clay catalyst produced the highest conversion of palmitic acid at 42%, while c-K-clay produced the highest conversion of oleic acid and stearate at 30%. In addition, the density and water content of biodiesel catalyzed by K-clay and c-k-clay meet SNI standards. This finding has the potential to be further developed as a cost-effective catalyst based on natural resources in biodiesel production.

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INTRODUCTION

The paucity of energy sources derived from fossil fuels motivates the exploration for sustainable energy sources. Biodiesel emerges as a viable resolution as it addresses the issue of fuel scarcity and exhibits enhanced environmental compatibility by generating significantly fewer emissions. Biodiesel could potentially be synthesized utilizing a wide range of feedstocks, such as various vegetable oils, animal fats, and even algae. However, because of the extravagant cost linked to biodiesel production, the use of waste-based feedstocks like waste palm oil has emerged alternative (Ahmadi et al., 2019; Hosseinzadeh-Bandbafha et al., 2022; Singh et al., 2021). The prevailing and most elementary approach for biodiesel synthesis involves the process of transesterification facilitated by a catalyst (Amirthavalli et al., 2022; Astam et al., 2020; Ghosh & Halder, 2022).

Heterogeneous catalysts are favored over homogeneous catalysts owing to their facile isolation from the resultant reaction products. Nevertheless, the primary challenge impeding the utilization of heterogeneous catalysts in biodiesel production is the exorbitant expense associated with them. Consequently, an exploration for affordable precursors exhibiting commendable catalytic properties becomes imperative to curtail production costs. Clays, in their unadulterated or modified states, represent natural substances that exhibit the potential to facilitate diverse industrial and laboratory processes on account of their convenient accessibility, economical nature, non-toxic character, and robust thermal and mechanical stability (Mohadesi et al., 2022; Syukri et al., 2022; Wang et al., 2022).

Natural clay minerals are typically characterized by compositional and particle size heterogeneity. Variations in mineral composition give rise to distinctive material properties, such as surface area and adsorption capacity. Among the clay minerals, kaolinite prevails as the most prevalent type. The hydroxyl group within kaolinite stands out as the most reactive functional group, enabling its involvement in numerous chemical reactions and ion exchange processes (Sihvonen et al., 2018; Zhang et al., 2018). Consequently, in order to enhance the commercial viability of these natural clay minerals and exploit their suitability across diverse applications, the challenge lies in devising an economical and efficient method to separate clay minerals from other coexisting minerals (Zhou et al., 2016). Among the simplest techniques for separation is fractionation based on particle size, accomplished through the addition of a dispersing agent (Silva-Valenzuela et al., 2018). This process relies on the interplay of electrostatic forces, whereby mineral particles exhibit distinct dispersion and aggregation behavior, thereby enabling the separation of specific mineral fractions (Chen & Peng, 2018; Du et al., 2021). The significance of this separation technique is the ability to obtain purer kaolinite mineral, subsequently facilitating its implementation as a catalyst.

Therefore, in an effort to find a cheaper catalyst to reduce the price of biodiesel production, in this research, kaolinite was separated from natural clay using a fractionation method with the help of NH_4Cl as a dispersing agent. This treatment is expected to produce a catalyst that has appropriate material characteristics so as to support better performance in catalyzing the transesterification reaction of WCO into biodiesel.

METHOD

Materials

The material used in this research is clay from an area in Solok Regency, West Sumatra, Indonesia. Waste Cooking Oil (WCO) as a source of triglycerides is obtained from the remains of three times frying, distilled water, ammonium chloride (Sigma Aldrich), and methanol (Merck).

Clay Sample Preparation

A total of 500 g of clay samples were soaked in distilled water for 24 h. Then, the clay is filtered using filter paper. The clay residue was separated and dried at 105 °C for 3 h. After that, the clay was crushed and sieved with a 90 µm sieve. The sample was named h-clay (heated-clay) (Syukri et al., 2020).

Kaolinite Fraction Treatment

A total of 20 g of h-clay was put into a beaker. Then, 40 mL of NH_4Cl 5% was added to the beaker and continued with magnetic stirring for 15 min. The stirred mixture was left for 4 days. After settling, the precipitate obtained is separated from the suspension by decantation. The suspension was filtered using Whatman No. 1 filter paper and then dried in an oven at 105 °C. The dried kaolinite fraction sample was named K-clay (Negara & Simpen, 2016).

Thermal Modification of Clay Mineral Fractions

The kaolinite fraction was thermally activated by calcining at 850 °C for 4 hours. After that, the sample was left at room temperature and then ground (Admi *et al.*, 2020). The sample was named c-K-clay (calcined-K-clay). All catalyst samples were characterized by X-ray diffraction (XRD), X-ray Fluorescence (XRF), and Laser Particle Size Analyzer (LPSA).

Transesterification of Waste Cooking Oil

The used cooking oil that will be used in the transesterification reaction is filtered first to remove small particles that contaminate the oil. After that, the water content in the oil is removed by heating the oil at a temperature of 110 °C until the water bubbles disappear. The used cooking oil was then characterized by GC-MS. The transesterification process of used cooking oil is carried out using the reflux method where a 250 mL three-neck flask is equipped with a condenser and thermometer. The molar ratio of used cooking oil and methanol used in this research was 1:6, and the amount of catalyst used was 3% (w/w). Initially, methanol was added to the h-clay, K-clay, and c-K-clay catalysts then heated to 50 °C with continuous stirring. After that, 30 mL of used cooking oil was added to the three-neck flask. The transesterification reaction was carried out for 3 hours at a temperature of 70 °C with a stirring speed of 500 rpm. The biodiesel product is separated from glycerol using a separating funnel. Biodiesel is washed with hot distilled water (50 °C) with a volume of 1:1 and homogenized for 5 minutes to form a white liquid. The main chemical components contained in the product were analyzed by GC-MS (Syukri *et al.*, 2022).

RESULTS AND DISCUSSION

Mineral Types and Crystal Size Analysis

XRD analysis was carried out to determine the type of minerals contained in the clay samples. The XRD diffractogram of clay sample is shown in Figure 1.

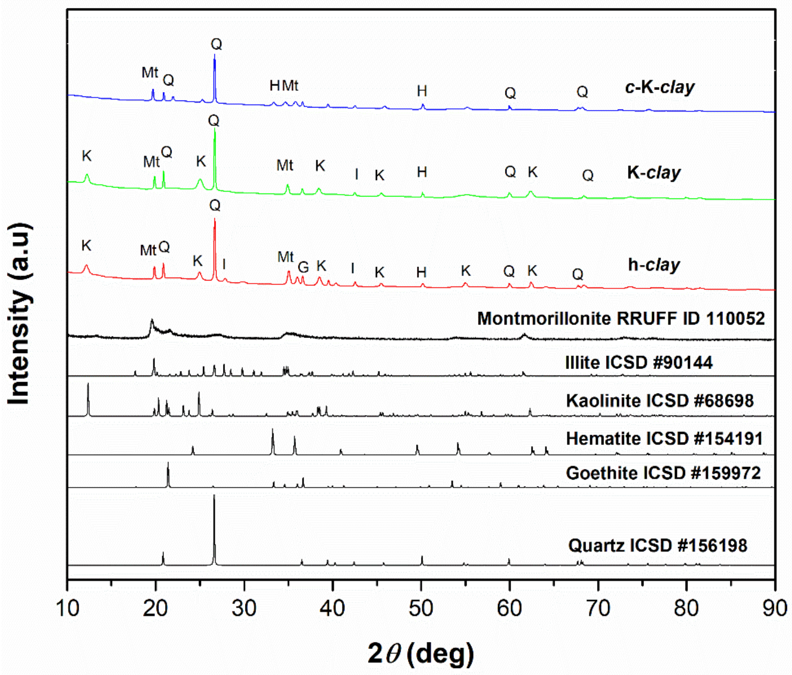

Figure 1. Comparison of XRD diffractograms of catalyst samples (K: kaolinite; Mt: Montmorillonite; Q: Quartz; I: Illite; G: Goethite; and H: Hematite)

Based on Figure 1, it can be observed that the clay sample contains a mixture of several types of minerals. The content of h-clay clay is the minerals quartz, kaolinite, montmorillonite, illite and iron oxide in the form of goethite and hematite. After the fractionation process, the clay samples showed a reduction in the types of minerals that could be observed, so that the presence of the kaolinite fraction became quite dominant. This indicates that the fractionation stage carried out has separated some minerals with larger particle sizes. The crystallinity of fractionated minerals also experienced an increase marked by an increase in the intensity of several kaolinite peaks, namely in the 2θ 12.2439° area from 103 to 108 and at 25.0095° from 95 to 125. This increase in intensity may indicate that the mineral obtained has a higher relative crystallinity (Pleşa Chicinaş et al., 2018). Apart from that, quartz minerals also experience a decrease in relative intensity after the kaolinite fractionation stage, which indicates the composition of the mineral may have been reduced (Andrade et al., 2019).

During the separation of the kaolinite and montmorillonite mineral fractions, electrostatic interactions and ion exchange occur between the clay components and the dispersing solution. In kaolinite fractionation, NH_4^+ ions from NH_4Cl can enter the kaolinite interlayer space which causes intercalation due to ion insertion (Lagaly et al., 2013). Intercalation in the kaolinite structure can cause swelling so that the interlayer space increases. This is due to the disruption of hydrogen bonds and Van der Waals forces that connect the layers of the kaolinite structure. NH_4^+ ions undergo cation exchange with cations around the interlayer space. The presence of Cl^- ions around the hydroxyl group can weaken hydrogen bonds between layers because the position of Cl^- ions is closer than oxygen in the tetrahedral layer. The interaction of kaolinite minerals with NH_4Cl is illustrated in Figure 2.

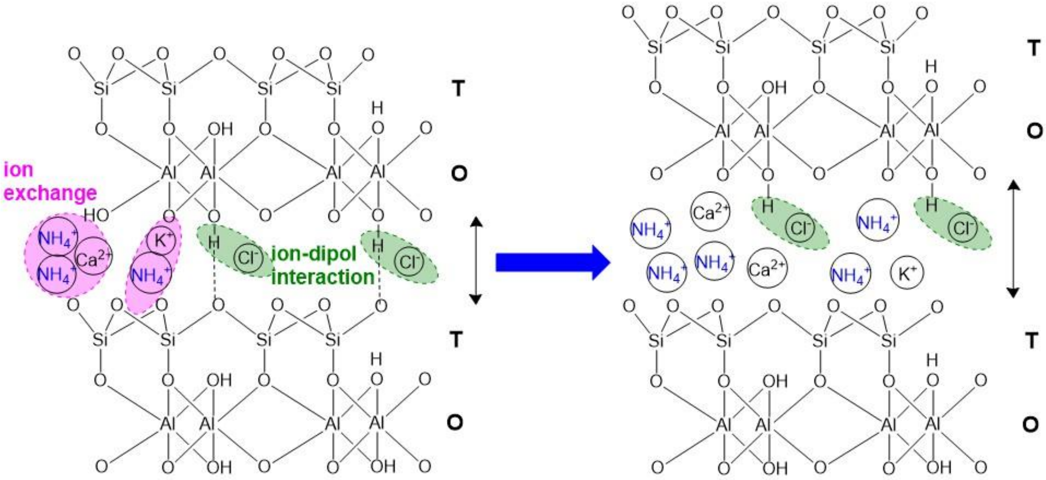

Figure 2. Illustration of the interaction of the mineral kaolinite with NH4Cl

After the calcination stage, several mineral peaks such as iron oxide and kaolinite also decreased in intensity and some peaks were even no longer found. The color of clay can change during calcination due to changes in the oxidation number of elements such as Fe, or the loss of some structural iron from the cristae structure. These results are also in line with research reported by Zheng et al. (2022) which showed a change in clay color from brown to reddish brown after calcination (Zheng et al., 2022). Fe(III) is formed from the transformation of goethite (FeO(OH)) into hematite (Fe_2O_3). The presence of a hematite peak in calcined clay was found at an angle of 2θ 34.6323° in c-K-clay. Apart from that, several kaolinite peaks also experienced a decrease in intensity. This decrease is thought to be due to kaolinite transforming from the crystalline phase to the amorphous metakaolin phase, resulting in the loss of the characteristic peak of kaolinite (Kassa et al., 2022). In the diffractogram, the disappearance of the kaolinite peak in the area 2θ 12.1725; 24.9475 and 62.3981° (ICSD #156198). The formation of the metakaolin phase is caused by the loss of –OH groups on the surface and the rearrangement of the Si and Al atoms, which causes octahedral Al reduction (Johnston et al., 2022). The conversion process of kaolinite into metakaolin is illustrated in the reaction provided.

$$2SiO_2.Al_2O_3.2H_2O \xrightarrow{650\ ^oC-\ 850\ ^oC} 2SiO_2.Al_2O_3 + 2H_2O$$

Based on the XRD diffractogram as seen in Figure 1, the crystal size of each peak of the kaolinite and montmorillonite minerals was calculated to obtain the average crystal size of each clay sample and the data are summarized in Figure 3.

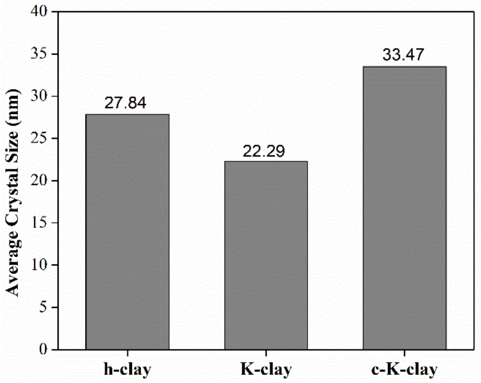

Figure 3. Average crystal size of the catalyst

In K-clay, the kaolinite mineral analyzed is smaller than the kaolinite mineral found in h-clay. A different phenomenon occurs when clay is subjected to thermal treatment, where the average crystal size for each mineral fraction increases. The development of coarser particles at 850 °C may be the result of fraction agglomeration due to sintering phenomena or particle expansion due to de-hydroxylation of clay minerals (Msinjili et al., 2019). These results are in line with those reported by Yanguatin et al. that calcination at a temperature of 550 °C results in an increase in particle volume because the increase in temperature produces dehydroxylated kaolinite particles which tend to aggregate so that the particle size increases (Yanguatin et al., 2019).

Oxide Composition

XRF analysis in this study was carried out to determine the oxide composition contained in the clay samples as shown in Table 1. The content of the clay samples was dominated by alumina (Al_2O_3), silica (SiO_2), and hematite (Fe_2O_3), as well as several other oxide compounds in small quantities.

Table 1. Oxide composition of catalyst

Oxide (%)	***h-clay***	**K-*clay***	***c*-K-*clay***
Al_2O_3	26.471	26.746	28.271
SiO_2	51.374	46.027	52.098
P_2O_5	3.497	3.961	2.965
K_2O	3.019	3.056	2.683
CaO	0.719	0.817	0.583
TiO_2	1.778	1.952	1.616
V_2O_5	0.051	0.051	0.044
Fe_2O_3	12.268	14.072	10.976
ZnO	0.024	0.03	0.021
SrO	0.051	0.065	0.049
ZrO_2	0.112	0.127	0.102
Ag_2O	0.533	0.349	0.502
PbO	0.004	0.003	0.003
Si/Al ratio	1.65	1.46	1.56

The Si/Al ratio of clay that has been treated with fractionation is generally reduced compared to the Si/Al ratio of h-clay. This may happen because the separation process carried out has separated a number of quartz contained in the clay causing the SiO_2 content to decrease so that the Si/Al mole ratio decreases. After the clay mineral fraction was calcined, what was interesting was that the Si/Al ratio experienced a slight increase. This is thought to be due to thermal treatment at high temperatures removing some of the oxide content in the clay which is indicated by the reduction in the percentage of several oxides such as P_2O_5, K_2O, CaO, TiO_2, and several other oxides so that the percentage of SiO_2 relatively increases.

Particle Size Analysis

This analysis was carried out to determine the particle size of the clay sample and changes in particle size that might occur when the clay sample was separated. The results of particle size measurements for each catalyst sample are summarized in Table 2.

Table 2. Characteristics of particle size distribution parameters of catalyst samples

Sample	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)	D_{av} (µm)
h-clay	0.71	6.53	59.88	27.61
K-*clay*	0.63	5.38	45.75	21.09
c-K-clay	6.43	18.33	52.25	25.62

Based on Table 2, it appears that there was a decrease in the average particle size of the clay samples after the treatment was given. However, in this study, the h-clay and K-clay samples showed large differences between D10, D50, and D90, indicating that the samples had very diverse particle sizes. In addition, there was an increase in particle size again after the calcination process. This correlates with the crystal size data in Figure 3 which is thought to have increased due to the sintering effect during calcination (Msinjili et al., 2019).

Catalytic activity assay

The catalytic activity test of the catalyst in this research was carried out on the transesterification reaction of used cooking oil. Based on the analysis that has been carried out, the main components of used cooking oil used are oleic acid (49.32%), palmitic acid (33.49%), and stearic acid (2.32%). The percentage conversion of fatty acid components in used cooking oil by each catalyst is shown in Figure 4.

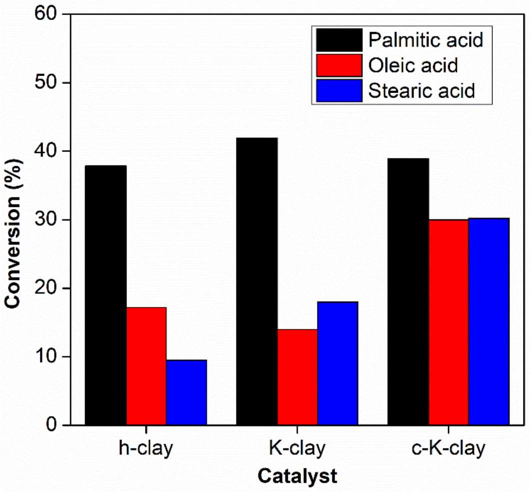

Figure 4. Percent conversion of fatty acids produced by h-clay, K-clay, and c-K-clay catalysts

Based on Figure 4, it can be observed that there was an increase in the total conversion of fatty acids catalyzed by the catalyst after being treated with both fractionation and calcination. The highest conversion of palmitic acid was found on the K-clay catalyst, while for the other two fatty acids, namely stearic and oleic, the highest was on c-K-clay. From these data, it can be assumed that the fractionation carried out has increased the selectivity of the catalyst for the conversion of palmitic and stearic acids. This is also supported by the characteristics of the K-clay catalyst which has the smallest crystal size, average particle size and Si/Al mole ratio among the two other catalysts which will play a role in the catalytic activity of the catalyst. Smaller particle size will correlate relatively with a larger surface area to facilitate the adsorption reaction of reactants on the catalyst surface (Nufida et al., 2014).

The low Si/Al mole ratio is related to the amount of negatively charged octahedral aluminate which can act as a Brønsted acid site due to the large number of metal ions bound to this site (Cheng et al., 2019). Meanwhile, in the c-K-clay catalyst a different phenomenon occurs where the catalyst characteristics such as crystal size and average particle size are the largest. Thus, the superiority of the c-K-clay catalyst may be due to the calcination process that has changed kaolinite into its amorphous phase, namely metakaolin, which is more catalytically active. During calcination, Lewis acids and bases can form on exposed alumina surfaces. When heated to about 100 to 150 ºC, water molecules decompose leaving some hydroxyl groups (OH^-) on the surface and these can act as Brønsted acids. An increase in higher temperature condenses the adjacent OH^- group to liberate H_2O resulting in an open Al^{3+} Lewis acid site as well as an O_2^- Lewis base site (Gbarakoro et al., 2018).

Analysis of the physical properties of biodiesel products is carried out through density and water content tests which are shown in Table 3.

Table 3. Physical properties of biodiesel

Physical properties	**SNI (7182: 2015**	**Catalyst**		
		h-clay	**K-*clay***	**c-K-*clay***
Density (g/cm^3)	0.85-0.89	0.87	0.87	0.88
Water content (%)	0.05	0.06	0.05	0.02

Based on the provided data, the obtained product density, specifically ranging from 0.87 to 0.88 g/cm^3, falls within the acceptable range for biodiesel as specified in the SNI guidelines (0.85-0.89 g/cm^3). Consequently, it can be concluded that the product complies with the prescribed density standards for biodiesel. The significance of density lies in its influence on fuel quality, particularly its impact on fuel atomization during the combustion process (Anwar et al., 2018). It is noteworthy to mention that a higher fuel density can result in viscosity issues in engines (Osorio-González et al., 2020). Furthermore, the water content present in fuel plays a crucial role in determining fuel quality (Tsoutsos et al., 2019). The presence of free water within the storage tank can foster the growth of biological organisms, leading to the corrosion of metals, especially iron and steel (Živković & Veljković, 2018). Additionally, the formation of sludge and slime can occur, potentially causing blockages in the fuel filter and fuel lines. Ultimately, this can cause detrimental effects on the vehicle's fuel injection system. In the study at hand, it is observed that the water content value for biodiesel catalyzed by K-clay and c-K-clay adheres to the SNI standards.

CONCLUSION

In this study, efforts have been made to separate kaolinite minerals from natural clay and activate them thermally. After the fractionation process, the crystallinity of the fractionated minerals experienced an increase marked by an increase in the intensity of several kaolinite peaks, namely in the 2θ 12.24° area from 103 to 108 and at 25.00° from 95 to 125. Thermal modification caused the loss of several kaolinite peaks in the area. 2θ 12.17°; 24.94° and 62.39° and the peak of goethite in h-clay in the 2θ area 36.58°. The Si/Al ratio decreases after the fractionation and calcination processes. Average particle size of h-clay decreased from 27.61 µm to 21.09 µm in K-clay, which indicates that the fractionation process has been able to separate a number of minerals with larger sizes. The fractionation and calcination stages carried out showed an increase in fatty acid conversion in WCO. The K-clay catalyst produced the highest conversion of palmitic acid at 42%, while c-K-clay produced the highest conversion of oleic acid and stearate at 30%. The aforementioned discovery has the capability to be expanded upon as an economical catalyst, utilizing renewable resources, within the realm of biodiesel manufacturing. For further research, optimization can be carried out to find optimum conditions that can produce better activity and selectivity.

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