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Performance Comparison of Heterogeneous Catalysts based on Natural Bangka Kaolin for Biodiesel Production by Acid and Base Activation Processes

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Abstract. This study is aimed to evaluate efficiency low-cost natural kaolin from Bangka island as a catalyst to produce biodiesel (fatty acid methyl ester, FAME) via the transesterification reaction using the cooking oil as a model of free fatty acids (FFA) source. Heterogeneous catalysts of the natural kaolin were prepared by an activation process using base (1-2 M NaOH) and acid (1 M HCl) solution. The base and acid activated kaolin are labelled as Kb1M, Kb2M, and Ka1M, respectively. The quality of biodiesel was analyzed according to the SNI 04-7182-2015 method, the American Society for Testing and Materials (ASTM) D 6751, and the Europäische Norm (EN) 14214, while the composition of biodiesel was determined using gas chromatography-mass spectrometry (GC-MS) analysis. Among the activated kaolin, the Kb2M showed the best heterogenous catalyst performance, producing 96.3% methyl ester with a yield of 69.4%. The highest FAME conversion was achieved using the Kb1M catalyst at 79.1% with a mole ratio of cooking oil to methanol being 1:3, whereas the lowest FAME conversion, 72.0%, was obtained using the Kb2M catalyst with a mole ratio of cooking oil to methanol being 1:6. Overall, the Kb2M showed the best efficient catalyst, while the Ka1M showed the lowest catalytic performance.

Keywords: Acid; Base; Biodiesel; Heterogenous Catalyst; Kaolin

1. Introduction

Exploring new catalyst materials to meet the growing demand for renewable and fossil energy has become increasingly important for energy production. Catalysts play a

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crucial role in reducing activation energy and shifting the position of chemical equilibrium, allowing reactions to reach completion and produce the desired product. For the case of biodiesel production, homogeneous base catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), and also alkoxide solutions are employed. However, homogeneous catalysts are reported to affect corrosion in the reactor, and also present challenges for catalyst recycling (Yang *et al.,* 2017). On the other hand, heterogeneous catalysts have also been explored to reduce the cost of biodiesel production (Carmo-Jr *et al.,* 2009).

Heterogeneous catalysts possess different phases between reactants and products. These catalysts have various advantages such as being environmentally compatible, non-corrosive, easy to separate from reactants, and facile to regenerate (Guan *et al.,* 2009). It is noted that heterogeneous catalysts can promote the transesterification of triglycerides for biodiesel production (Aziz *et al.,* 2017; Yan *et al.,* 2010). Efforts to reduce the cost production of biodiesel rely on the availability of abundant and cheap raw material catalysts, sources of free fatty acid, proper reactor design, method, and type of reaction process (transesterification or esterification).

Natural kaolin occurs over several regions of Indonesia, such as West Kalimantan, South Kalimantan, Bangka Belitung, Sulawesi, and Java with a total deposit of approximately 66.21 million tons (Subari, Wenas and Suripto, 2008). Natural Bangka kaolin has been used as an adsorbent for the adsorptive removal of antibiotic rifampicin from an aqueous solution (Majid *et al.,* 2023). On the other hand, the application of Indonesian kaolin from Bangka has also been reported as an adsorbent for adsorption of negatively charged acid blue 25 and acid 1 (Asbollah *et al.,* 2022). Natural kaolin has also been reported as a catalyst for transesterification reactions (Ali et *al.,* 2018; Đặng, Chen, and Lee, 2017). With its high surface area, porosity, and composition, along with its low cost, the natural kaolin highlights its potential as an effective raw catalyst material. For instance, graphene oxide (GO) enriched natural kaolinite clay as catalyst for biodiesel production has been reported by Syukri *et al.* (2020). GO is a single atomic layer of graphite oxide that has a high specific surface area with a complex mixture of oxygen at the edges and basal planes (Kusrini *et al.,* 2020a; Nasrollahzadeh *et al.,* 2014). GO has a Bronsted acid side which is important for esterifying the free fatty acid (FFA) content in oil (Atadashi *et al.,* 2013). It was reported that metal oxide/GO composites increased the mechanical strength of heterogeneous catalysts (Marso *et al.,* 2017).

To increase the quality and ability of natural Bangka kaolin as a heterogeneous catalyst for biodiesel production, activation of kaolin using base and acid treatments is needed to enhance the active sites of the natural kaolin. This process is able to enlarge its surface area and remove impurities on the surface of natural kaolin. Base treatment for the activation can improve crystallinity of the natural kaolin (Belver, Bañares-Muñoz, and Vicente, 2002). The catalyst that was activated using base treatment showed 4,000 times faster than those found for the acid catalyst under a similar amount of catalyst for the transesterification reaction (Fukuda, Kondo, and Noda, 2001). New catalyst materials for energy production and/or other applications have attracted many researchers to address the need for clean energy (Arnas, Whulanza, and Kusrini, 2024; Whulanza and Kusrini, 2024).

Biodiesel is an alkyl ester with other non-toxic compounds. It is a mixture of long-chain fatty acid methyl esters (FAMEs) or ethyl esters (FAEEs). Biodiesel can be produced by either the transesterification of animal fats, vegetable oils, or used cooking oil or esterification of free fatty acids (FFAs) (Dang, Chen and Lee, 2013) in the present of alcohol compound such as methanol (CH_3OH) or ethanol (C_2H_5OH). Usually, production of biodiesel through esterification and/or transesterification reactions that are assisted by an acid or base catalyst (Maneerung *et al.,* 2016). Biodiesel can be obtained by a transesterification reaction, whereas the green diesel as the second generation of diesel can be produced through hydrodeoxygenation reaction (Aisyah *et al.,* 2023). Apart from containing esters, vegetable oils and animal fats also contain small amounts of FFA. The presence of FFA in the transesterification reaction with an alkali catalyst needs to be considered. The maximum FFA content in vegetable oil when using a base catalyst is approximately 3%, if it exceeds this level the reaction cannot occur, as reported by Atadashi *et al.* (2013). This is because free fatty acids will react with an alkali catalyst to form soap. Thus, before the transesterification reaction was carried out, the oil must be first pretreated to reduce the FFA content. After the transesterification reaction was complete, two products will be obtained, namely biodiesel (methyl ester) and glycerol.

Although sources of biodiesel can be vegetable oils such as palm oil, coconut oil, corn oil, soybean oil, sunflower seed oil, and rapeseed oil, non-edible oils such as jatropha curcas, pongamina pinnata, sea mango, palanga, and/or tallow oil are more preferred (Leung, Wu and Leung, 2010). Many countries use vegetable oils as the main ingredient for making biodiesel because the properties of the biodiesel produced are close to those of diesel fuel (Gui *et al.,* 2008). Biodiesel has advantages compared to diesel fuel from petroleum. The advantages of biodiesel are an environmentally friendly fuel because it produces much better emissions (free sulfur and smoke number), and higher cetane number (>50). Thus, the combustion efficiency of biodiesel is better than that of crude oil, displays lubricating properties for engine pistons, and improves vehicle life, safe storage, and transport, including its non-toxic and biodegradable properties (Balat and Balat, 2010). Biodiesel is an ideal fuel for the transportation industry because it can be used in various diesel engines, including agricultural machines.

Thus, to observe the potential of Bangka kaolin as a heterogeneous catalyst for biodiesel production, this natural kaolin was activated using a base solution (1–2 M NaOH) and in acid (1 M HCl) media. Both heterogeneous catalysts were evaluated and tested for biodiesel production, where cooking oil was used as a source of free fatty acid (FFA) for biodiesel production. Kaolin was chosen as the model clay for the development of the efficacious heterogeneous catalyst in production of biodiesel through the catalyzed transesterification reaction.

2. Methods

2.1. Materials

Natural kaolin was originated from Bangka, Belitung Island, Indonesia. Palm cooking oil is a commercial product containing FFA <2%. NaOH and HCl were purchased from Merck (Germany). All the chemicals were used without any further purification.

2.1.1. Pretreatment of natural kaolin

50 g of Bangka natural kaolin (150 mesh) was mixed with 400 mL of distilled water and stirred using a magnetic stirrer until the mixture became homogeneous. The natural kaolin was then separated from this mixture using the centrifugation technique. The clean natural kaolin was dried in an oven at 105°C for 2 h. Furthermore, a dried natural kaolin was calcined at 500°C for 6 h to form a metakaolin. Then, a metakaolin was used to produce a heterogeneous catalyst in subsection 2.3.

2.2. Activated heterogeneous catalysts using base and acid treatments

Each sample of metakaolin (3.7 g) was mixed with at 1 M or 2 M NaOH solution, along with magnetic stirring at 500 rpm for 6 h at room temperature. Then, the base metakaolin obtained by using 1 M and 2 M NaOH in the respective order were separated from the NaOH solution using a centrifugation process for 10 minutes at a speed of 2500 rpm. The solid base metakaolin was washed using distilled water, and it was dried in an oven at 105°C for 2 h. Each base metakaolin product was calcined in the furnace at 500°C for 6 h. Finally, both heterogeneous catalysts were produced and named as follows: base-activated kaolin using 1 M NaOH (Kb1M) and base-activated kaolin 2 M NaOH (Kb2M). A similar procedure was used to produce acid-activated kaolin using 1M HCl solution, which was named as acid-activated kaolin 1 M (Ka1M).

2.3. Performance test of heterogeneous catalysts for biodiesel production

The palm cooking oil was used as a model source of oil. This oil was heated at 65°C. A mixture of methanol and catalyst with a ratio of 1:3 was added into the heated cooking oil and stirred using magnetic stirring at 500 rpm and 60°C for 60 minutes. The ratio of catalyst to cooking oil is 3 wt.%. Then, the mixture was put in the separated funnel and kept for 6 h until 2 layers formed, where the biodiesel (fatty acid methyl ester, FAME) product was obtained. FAME was washed using a warm water until the color of the water was clean. A product of biodiesel was heated at 110°C to remove the remaining water. Finally, the biodiesel product was kept for further characterization according to the SNI 04-7182-2015 method.

2.4. Characterizations

The heterogeneous kaolin-based catalysts were characterized using a scanning electron microscopy-energy dispersive X-ray (SEM-EDX), X-ray diffraction (XRD), and Fourier transform infra-red (FTIR) spectroscopy. XRD characterization was carried out to determine the size and crystalline structure of the catalyst. FT-IR spectral characterization was carried out to determine the types of functional groups of samples. The crystallite sizes of catalysts were determined using the Debye-Scherrer (Equation (1)). Due to limited access to instruments and funding for this study, spectral characterization (FTIR, XRD, and SEM-EDX) were conducted for both Kb1M and Kb2M heterogeneous catalysts.

$$\mathrm{L} = \frac{\mathrm{K}\lambda}{\beta\cos\theta} \tag{1}$$

where L is crystallite size, λ is wavelength of diffraction light (0.15406 nm), β: full width at half maximum (FWHM) in radians, K is constant (0.89), and θ is diffraction angle.

The results of the transesterification reaction, namely FAME were analyzed using GCMS. The quality of FAME was determined using the SNI quality standards 04-7182-2015 method, the American Society for Testing and Materials (ASTM) D 6751, and the Europäische Norm (EN) 14214, including density, viscosity, and FAME %. The FAME yield was calculated using an equation that was reported by Soetaredjo *et al.* (2011). FAME % yield and % conversion based on the GC-MS analysis were also calculated using Equations 2 and 3;

$$\%yield = \frac{Weight\ of\ biodiesel\ x\ total\ weight\ of\ \%FAME}{Weight\ of\ cooking\ oil} x\ 100 \tag{2}$$

$$Conversion\ = \frac{Weight\ product}{Weight\ of\ feed} x\ 100\% \tag{3}$$

3. Results and Discussion

3.1. Preparation of kaolin to metakaolin

Pre-treatment of kaolin aims to reduce impurities and eliminate the water content present in natural kaolin. No color change was observed in the kaolin before and after calcination at 500°C. At a calcination temperature of 500°C, the bond between the hydroxyl groups attached to the octahedral alumina on the kaolin surface weakens and breaks which is called pre-dehydroxylation. A dehydroxylation reaction occurred, where the hydroxyl group bonds in natural kaolin absorb energy which then decomposes. Removal of nearly all hydroxyl groups from natural kaolin causes the crystal structure of kaolin to break down, which then becomes amorphous. This amorphous phase of kaolin is called a metakaolin. A comparison of the color of kaolin (150 mesh), heated in an oven and after calcination at 500°C is shown in Figure 1A-C.

Figure 1 Preparation of (A) natural kaolin 150 mesh, (B) kaolin after oven heating, and (C) kaolin after calcination (metakaolin)

3.2. The physical properties of activated Kaolin

Comparison of the physical properties of activated kaolin using 1M or 2M NaOH, the kaolin was separated from the NaOH solution after washing with distilled water. The dried kaolin and the calcined kaolin (metakaolin) are shown in Figure 2A-E.

All heterogeneous catalysts were produced, namely Kb1M, Kb2M, and Ka1M. The addition of NaOH and HCl aims to dissolve silica and alumina from natural kaolin. NaOH acts as a metallizer and a base agent because the kaolin structure forms an excess negative charge on the aluminum ion in order to support cations that are needed outside the framework to neutralize its surface charge. The addition of NaOH as a mineralizer in the synthesis of kaolin catalysts due to the capacity of water as a solvent at high temperatures is often unable to dissolve substances in the crystallization process. The activation process can enlarge the pore size and open the pores of natural kaolin. On the other hand, the calcination process at the activation stage aims to ensure the formation of crystals on the kaolin surface. In general, the reaction mechanisms are illustrated in Equations (4) and (5);

$$2\ NaOH_{(aq)} + Al_2O_{3(s)} + SiO_{2(aq)} + 5\ H_2O_{(l)} \rightarrow 2\ NaAl(OH)_{4(aq)} + Si(OH)_{4(aq)} \quad (4)$$

$$2\ NaAl(OH)_{4(aq)} + 2\ Si(OH)_{4(aq)} \rightarrow [Na_2(AlO_2)_2(2SiO_2)\ .\ 8H_2O] \quad (5)$$

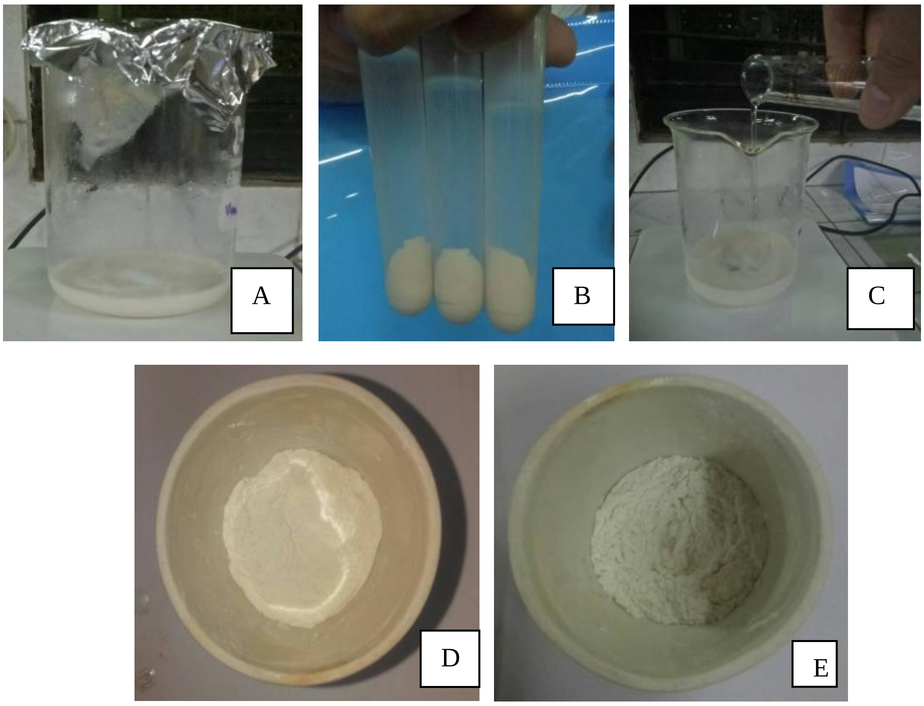
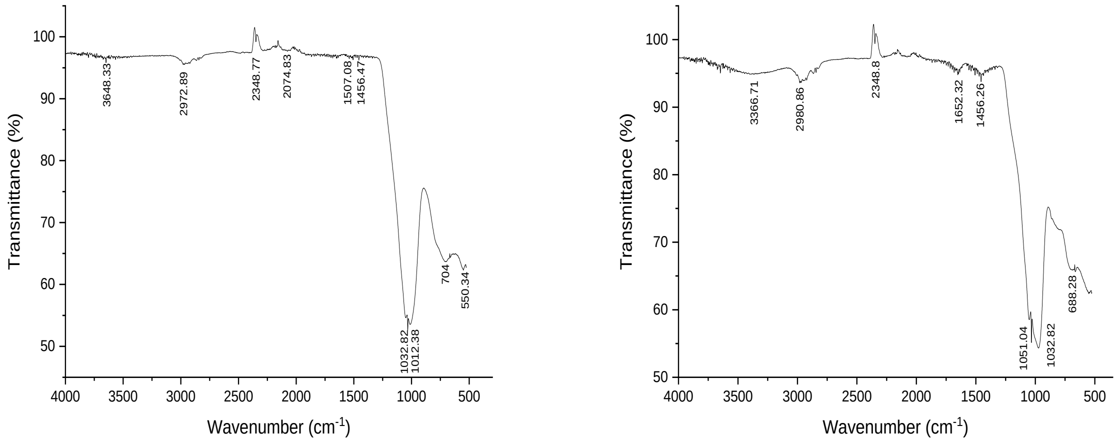


Figure 2 Comparison of the physical properties of (A) activated kaolin using NaOH (1M and 2M), (B) kaolin that was separated from the NaOH solution, (C) washing of kaolin using aquadest, (D) dried kaolin, and (E) calcined kaolin (metakaolin)

3.3. *FTIR spectral characterization*

FTIR characterizations were only carried out for 2 types of heterogeneous catalysts, namely Kb1M and Kb2M. The FTIR spectra of catalysts Kb1M and Kb2M are shown in Figure 3(A-B). Both FTIR spectra are not similar since the intensity of the absorption peaks show variability, as noted for the weak band at 3648 cm^{-1}, strong bands at 1032; 1012 cm^{-1} for Kb1M, and 3366 cm^{-1}, 1051; 1032 cm^{-1} for Kb2M. The Kb1M catalyst has an absorption peak at 704 cm^{-1}, showing the asymmetric stretching of Si-O-Si and Al-O-Al. The absorption bands at 1012 cm^{-1} and 1032 cm^{-1} indicate the presence of O-Si-O and O-Al-O asymmetric stretching vibrations of the aluminosilicate framework. One of the characteristics of zeolite A is having double rings which is revealed by the absorption for the IR band at 550 cm^{-1}. The peaks at 1456 cm^{-1} and 1507 cm^{-1} relate to the bending vibration of the Si-O-Si group. The band at 3648 cm^{-1} was observed for Kb1M, while the peak at 3366 cm^{-1} was observed for KB2M. This peak is assigned for the vibration of the hydroxyl (O-H) group. The IR band at 2972 cm^{-1} shows the Al-O-Na vibration. An IR band at 688 cm^{-1} shows the symmetrical Si-O and Al-O vibrations for the Kb2M catalyst.

For comparison purposes, the FTIR spectra of Kb1M and Kb2M are quite different than the FTIR spectra of zeolite A, as reported by Kusrini *et al.* (2024a; 2024b). Generally, the vibrational bands of zeolite A appeared at 2175, 1989, and 879 cm^{-1}, where the absorption peak at 879 cm^{-1} was attributed to the internal vibrations of Si-O and Al-O bonds and the asymmetric stretching within the tetrahedral zeolite structure (Kusrini *et al.*, 2024a; Kusrini *et al.*, 2024b).



(A) (B)

Figure 3 FTIR spectra of (A) Kb1M and (B) Kb2M catalyst materials

3.4. XRD characterization

XRD patterns of heterogeneous catalysts (Kb1M and Kb2M) are shown in Figure 4(A-B). Based on Figure 4(A), the XRD results of the Kb1M catalyst showed the appearance of XRD signatures at 2θ values of 10.15°; 12.44°; 21.65°; 23.98°; 27.1°; and 29.94°, which provide support of the formation of zeolite A. By comparison, the XRD result in Figure 4(B) for Kb2M showed the appearance of a band at 2θ = 25.28°, which indicates that quartz was still present. The dominant crystal structure is kaolin, while the Q peak in the form of quartz (SiO_2) is a crystalline phase only slightly observed in the XRD pattern, where the peak of SiO_2 occurs at 2θ = 26.61°. The formation of zeolite A is not supported by the Kb2M catalyst. Based on a calculation using the Debye-Scherrer equation (Equation 1), we obtained the crystallite sizes of the Kb1M and Kb2M catalysts. The crystallite size of Kb1M is larger (41.73 nm) compared to Kb2M (23.64 nm), as shown in Table 1. This size is smaller than those found by Kusrini *et al.* (2024b) with crystallite size of 49.22 nm and crystallinity of NaA is 99.73%.

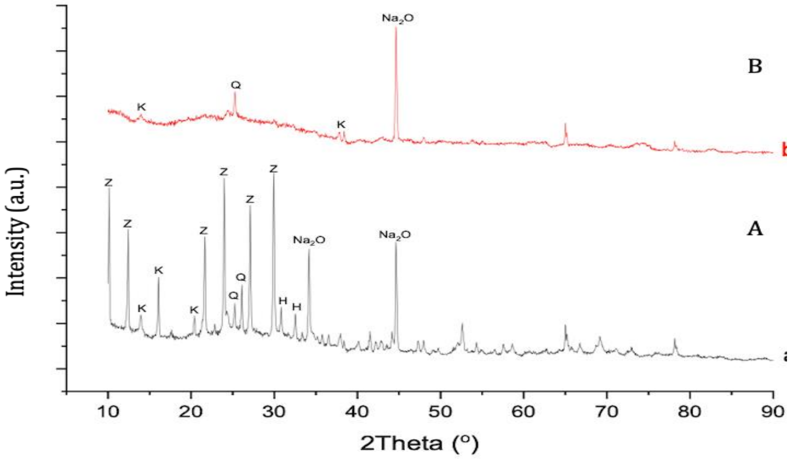


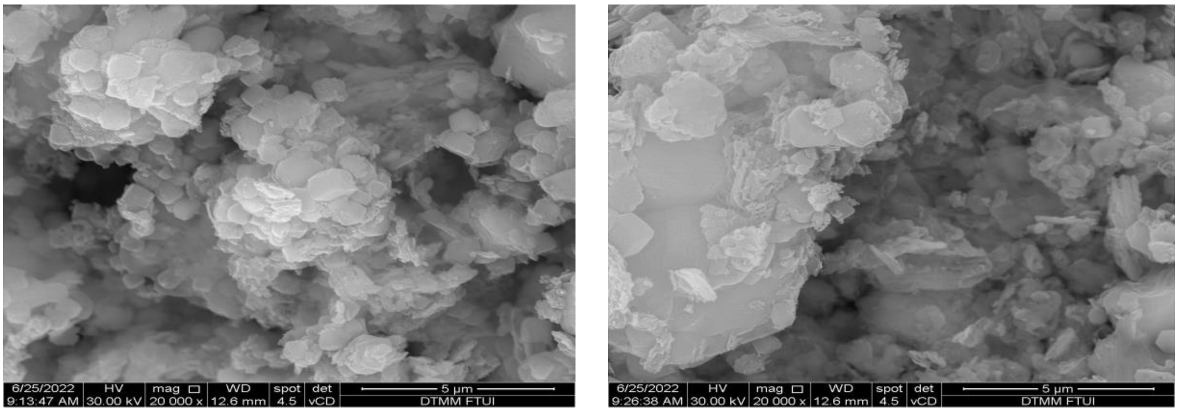
Figure 4 XRD patterns of the heterogeneous catalyst materials: (A) Kb1M, and (B) Kb2M, where K (kaolinite), Q (quart), and Z (zeolite A) are indicated

Table 1 Comparison of heterogeneous catalyst crystal size using Debye-Scherrer Equation

Type of catalyst	2θ (°)	FWHM (°)	Cos θ	Crystal size (nm)
Kb1M	29.94	0.19	0.966	41.73
Kb2M	25.29	0.29	0.976	23.64

3.5. SEM-EDX studies

Scanning electron microscopy (SEM) characterization was carried out to determine the morphology and surface structure of the catalysts. Based on Figure 5, the morphology of the Kb1M catalyst showed uniform cube-shaped crystals for zeolite A. In this study, the aim to obtain efficient catalysts from lost-cost natural kaolin, not to synthesize purposely the zeolites. However, the kaolin-derived catalysts possessed the characteristics of Na-zeolite A (NaA). This SEM image showed that zeolite A particles are cubic in shape with sharp edges. It is similar reported by Kusrini *et al.* (2024b), where the NaA has the morphology of a perfect cube with sharp cube edges, while zeolite A or Linde Type-A (LTA) is the result of the synthesis of alumina silicate minerals which have a cube morphology with blunter cube ends.



(a) (b)

Figure 5 SEM images of the catalyst materials: (A) Kb1M and (B) Kb2M with 20,000× magnification

From this study, the Kb1M catalyst has sharp edges with a cubic shape that resembles the NaA material reported by Kusrini *et al.* (2024a; 2024b). It is also similar to the results reported by Farghali, Abo-Aly, and Salaheldin (2021) where zeolite A has a uniform cube shape with an average particle diameter of 1 μm. The SEM results for the Kb2M catalyst showed a typical morphology of kaolinite in the form of a group of layered hexagonal sheets with heterogeneous sizes and a few typical zeolite cube crystals. This morphology can be attributed to an incomplete calcination process or imperfect grinding of the hexagonal sheets into cube crystals, and may also be influenced by the concentration of NaOH.

The EDX spectra of both heterogeneous catalysts of Kb1M and Kb2M showed the elements present on the sample surface, including C, O, Na, Al, and Si (Table 2). The presence of C in Kb2M may be due to impurities and/or other precursors. It is similar observed with NaA that reported by Kusrini *et al.* (2024a). The formation of heterogeneous catalysts using pre-treatment, calcination, and activation stages using NaOH solution ranged from 1–2 M, which gave rise to the formation of zeolite A. With the addition of NaOH, the Si/Al ratio of the Kb1M and Kb2M catalysts varied from 1.154 to 1.246 (see Table 2). The zeolite A morphology and the Si/Al ratio are comparable with results reported by Kusrini *et al.* (2020b). Na-zeolite A (NaA) reported by Kusrini *et al.* (2024b), the Si/Al rasio is 1.007. However, according Kusrini *et al.* (2024a), the Si/Al ratio is 2.469. The Si/Al ratio of zeolite A can differ due to the NaOH concentration, pre-treatment, size of kaolin, and the sequence of synthetic steps that follow the hydrothermal and calcination techniques.

Table 2 Compariosn of EDX compositional characterization of the heterogeneous catalysts (Kb1M and Kb2M) and NaA

Material	Element (*At %*)					Ratio	Reference
	C	O	Na	Al	Si	Si/Al	
Kb1M	-	46.89	11.96	18.32	22.83	1.246	
Kb2M	06.53	48.21	10.87	15.97	18.43	1.154	
NaA	-	39.49	9.21	13.46	14.76	1.097	Kusrini *et al.* (2020b)
NaA	3.147	40.217	11.303	12.96	32.003	2.469	Kusrini *et al.* (2024a)
NaA	-	39.49	9.21	13.46	13.55	1.007	Kusrini *et al.* (2024b)

3.6. Production of Biodiesel via a Transesterification Reaction

The Kb1M, Kb2M, and Ka1M materials as heterogeneous catalysts for biodiesel production using transesterification reaction were studied in detail. The acid number of cooking oil is 0.56 mg KOH/g. This value shows that the cooking oil as a model can be used directly to produce biodiesel via the transesterification reaction. If the value of acid numbers is high that can indicate high FFA levels, which can inhibit the biodiesel formation process. This can also lead to a saponification reaction. The variation of mole ratio of cooking oil:methanol used in the transesterification reaction are 1:3 and 1:6 to obtain the best ratio of cooking oil:methanol for biodiesel production. Furthermore, the palm cooking oil was heated at a temperature of 65°C to remove the water content contained in the oil. High water content can cause the reaction to undergo saponification, which causes a reduction of the methyl ester yield and challenges for separating glycerol from the methyl ester, including an increase in viscosity and emulsion formation. The catalyst content of 3 wt.% was used for the biodiesel production.

Initially, the process for the production of biodiesel was started by mixing heated cooking oil, methanol, and respective catalysts Kb1M or Kb2M in a reactor at a temperature of 60°C during a reaction time of 60 minutes. After the transesterification reaction, the process was complete, and the mixture was transferred to a separatory funnel to separate the formed phases. After separation from the separatory funnel, the biodiesel product was washed with warm water until the color of the water was no longer cloudy. Washing with the warm water prevents the precipitation of saturated methyl esters and the formation of emulsions. It is noted that the heterogeneous catalyst exhibits better reusability, multiple cycles, and easier separation compared to the homogenous catalyst. The major causes of catalyst deactivation can be occurred if the leaching of active sites, clogging of pore spaces of catalyst, the multiple cycles, and thus the performance of heterogeneous catalyst, were reduced. This condition is comparable with the biodiesel production that reported by Dang, Chen and Lee (2013). The palm oil produced the yield approximately 95% with the operation condition for biodiesel production after 2 h of reaction at 63°C (Dang, Chen and Lee, 2013). Almost 90% of triglycerides in palm oil was converted to biodiesel after 6 h of reaction at 50°C.

The temperature reaction in this study is similar to biodiesel production from palm fatty acid distillate (PFAD) using ZrO_2/bagasse fly ash catalyst with FFA esterification conversion of 90.6% as reported by Rahma and Hidayat (2023). They reported that the reaction temperature of 60°C, ratio of methanol to palm fatty acid distillate of 10:1, catalyst loading of 10 wt.% of PFAD, and reaction time of 2 h.

3.7. GC-MS characterization

GC-MS analysis was carried out to determine the composition of methyl esters contained in a biodiesel product. The identified methyl esters were compared with standard references, based on the respective retention time data which was confirmed by mass spectrometry from the GCMS results with a cooking oil:methanol mole ratio (1:3) and (1:6) (see Table 3). Kb1M catalyst produced 35.1% area of methyl ester at a mole ratio (1:3) and 86.5% at a mole ratio (1:6). As shown in Table 3, the Kb2M catalyst can produce 96.3% of the area of methyl ester with a mole ratio of cooking oil:methanol (1:6). Meanwhile, the Ka1M catalyst did not produce any area (0% based on GCMS results) for the methyl ester. This indicates that the Ka1M material cannot be used as a catalyst for biodiesel production via transesterification reaction since the acid cannot change FFA to FAME. Kaolin as catalysts in biodiesel production via transesterification reaction of vegetable oils in excess of methanol has been also reported by Dang, Chen, and Lee (2013). However, the conversion efficiencies were approximately 2.2 and 2.6%, respectively, for soybean oil and palm oil after 40 h of transesterification reaction (Dang, Chen, and Lee (2013).

As shown in Table 3, it can be seen that the highest FAME yield was 69.4% using Kb2M at a ratio of cooking oil: methanol (1:6). The best and optimum use of cooking oil:methanol mole ratio is at 1:6 ratio because it produces a large FAME yield. When compared to a 1:3 ratio, the FAME yield was 63.2% using Kb1M at a ratio of cooking oil:methanol (1:6) and 27.8% at a ratio of cooking oil:methanol (1:3). It is also comparable procedure with the transesterification reaction of blended oils at 60°C for 1 h, and the mole ratios of oil:methanol varied 1:3, 1:6, 1:9, 1:12, and 1:15 that reported by Wahyono *et al.* (2022). The oil: methanol mole ratios of 1:6 produced the best yield of 92.99% with the conversion of 99.58% mass according to the GCMS results (Wahyono *et al.,* 2022). Additionally, metakaolin was activated using a 1 M HCl solution. This process does not result in the production of FAME since the acid catalyst does not generate any fatty acids.

Table 3 Comparison of yield and conversion of FAME with a variable mole ratio of oil: methanol 1:6 and 1:3

Type of catalyst	The mole ratio cooking oil: methanol (1:6)			
	Yield FAME (%)	Weight (g)	Conversion (%)	Weight (g)
Kb1M	63.16	48.93	73.03	48.93
Kb2M	69.39	21.61	72.03	21.61
Ka1M	0		75.89	
	The mole ratio cooking oil: methanol (1:3)			
	Yield FAME (%)	Weight (g)	Conversion (%)	Weight (g)
Kb1M	27.80	53	79.10	53

The highest FAME conversion rate (79.1%) was achieved using Kb1M with a mole ratio of 1:3. On the other hand, the lowest FAME conversion rate was 72.0% using Kb2M with a mole ratio of 1:6. However, it is important to note that this conversion value alone does not determine the quality of the resulting FAME. This conclusion is supported by the GCMS results. It is also worth mentioning that transesterification reactions do not always yield biodiesel. Đặng, Chen and Lee (2017) reported the conversion yield of triolein to biodiesel increased up to 94.3% when the aging for time preparation of the zeolite Linde Type A (LTA)-kaolin catalysts were extended from 6 to 48 hours. The excess methanol for production of biodiesel using triglycerides as source is one of optimum condition chosen.

The physical properties of biodiesel products were analyzed, according to the Indonesian National Standard (SNI) number 7182:2015 method for biodiesel. Table 4 shows the density and viscosity of the synthetic biodiesel that is accompanied by standard data from SNI No. 7182:2015.

Table 4 Comparison of the physical properties of biodiesel using an oil: methanol ratio of 1:6

Parameter	Catalyst Type		SNI 04-7182-2015	ASTM D 6751	EN 14214
	Kb1M	Kb2M			
Density (kg/m^3)	895.2	898.1	850-890	900	860–900
Kinematic Viscosity at 40°C mm^2/s (CST)	31.85	38.65	2.3-6.0	5.0	3.50–5.0
Acid Value (mg KOH/g) (max)	2.4	2.2	0.4	0.5	0.50
Total glycerol (% mass) (max)	Not determined	Not determined	0.24	0.24	0.25
Methyl ester (% mass, min)	86.	96.3	96.5		96.5

The cooking oil employed has a density of 899 kg/m^3 and a viscosity of 48.62 cSt. A minor decrease in density occurs that was caused by the reaction of triglycerides in cooking oil with methanol. Thus, the triglycerides were converted into methyl esters. The characteristics of biodiesel products from this study were compared with the biodiesel quality standards of the American Society for Testing and Materials (ASTM) D 6751, Europäische Norm (EN) 14214 (European Committee for Standardization, 2002), and SNI 7182 (The National Standardization Agency of Indonesia, 2015). The viscosity of the biodiesel produced from the synthesis is relatively high and falls outside the acceptable range according to the SNI standard. However, the biodiesel products meet the requirements of ASTM D 6751 and EN 14214, primarily due to their acceptable density properties and percentage of methyl ester by mass. The high viscosity value is caused by the incomplete transesterification reaction and the large number of FFA with long carbon chains in the biodiesel product. The high mechanical viscosity of biodiesel probably occurs due to incomplete glycerol separation.

Comparison of the biodiesel produced by the heterogeneous catalysts (Kb1M and Kb2M) are shown in Figure 6. The Kb2M catalyst showed the highest catalytic performance, which produced a methyl ester area of 96.3% with a yield of 69.4%.

On the other hand, the oxide lanthanides composites such as CaO/La$_2$O$_3$, MgO/La$_2$O$_3$, and CaO/CeO$_2$ were also reported and used as heterogeneous catalysts for biodiesel production. In this sense, the lanthanides as critical minerals and have many applications for petroleum productions, energy, catalyst, and antiamoebic activity (Kusrini *et al.*, 2024c). These oxides can increase the catalytic activity and stability, as they have much better resistance towards FFA in biodiesel reactions (Santoro *et al.*, 2016). Additionally, the clay was also reported as a catalyst which can improve for distributing lanthanides into the clay. It can be useful for increasing the number of active sites on a catalyst, thus the contact between the reactants and the catalyst will be greater and product formation will be faster. Biodiesel is one of renewable energy option that can be further produced to fulfil the need of energy in Indonesia. This fuel is economically viable and environmentally friendly (Ebrahimi *et al.*, 2024). These factors were attributed to the high energy density, biodegradability, a reliable supply chain, and non-toxicity. The main component of biodiesel is methyl esters that can derived from various biomass sources including non-edible oil, edible, waste, plant oils and/or and discarded cooking oils. This innovation can be more promising as Indonesia has enormous abundant resources for biodiesel production to reach the Golden Indonesian in 2045 and to reduce the energy crisis. This will become more pronounced by utilizing different kinds of heterogeneous catalysts found locally as resources to provide a renewable energy including biodiesel, jet fuel and/or biogasoline as an alternative energy now and in the future.

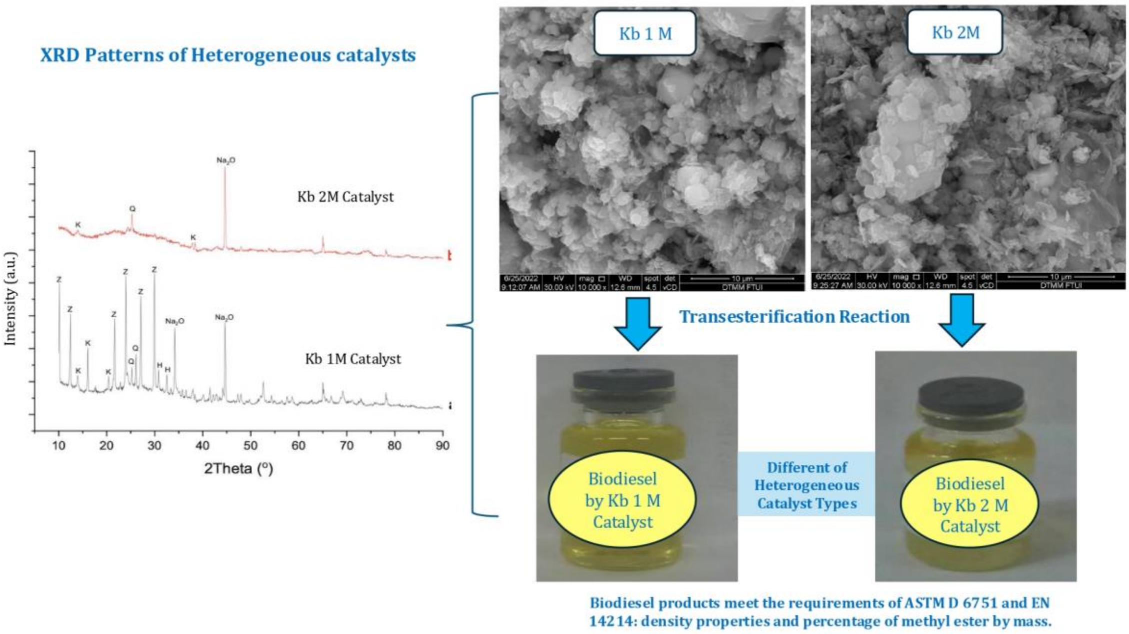


Figure 6 Comparison of biodiesel produced by heterogeneous catalysts of Kb1M and Kb2M. Operation condition at 60°C, reaction time of 60 minutes, and oil:methanol ratio of 1:6

4. Conclusions

In this study, application of low-cost natural kaolin as a catalyst to produce biodiesel (fatty acid methyl ester, FAME) via the transesterification reaction using the cooking oil as a model of free fatty acids (FFA) has been evaluated. Natural kaolin was calcined and activated using base (NaOH) and acid (HCl) additives in solution to produce heterogeneous catalysts that were used for biodiesel production. Unexpectedly, the activation leads the formation of zeolite A, so that the kaolin-derived catalysts possessed the characteristics of zeolite NaA. The Kb1M catalyst has NaA morphology, whereas the Kb2M catalyst shows partial morphology of zeolite A that still maintains the hexagonal sheets that are typical of kaolinite. The quality of biodiesel products does not fulfil the standard SNI 04-7182-2015, except for the methyl ester area, according to the results of this study. However, the biodiesel products are acceptable for ASTM D 6751 and EN 14214 mainly for the density properties and % mass of methyl ester. In future, the Kb2M catalyst can be optimized further to obtain the best catalyst and meet the SNI 04-7182-2015 standards across all parameters. On the other hand, further investigation can be continued to obtain the biodiesel and having favorable properties for ASTM D 6751 and EN 14214, thus it could be leveraged in industrial biodiesel production. The Kb2M catalyst has the highest catalytic performance, which produced a methyl ester area of 96.3% with a yield of 69.4%. Future research would be exploring alternative activation methods and scaling up production of biodiesel using kaolin, graphene, lanthanides and/or their composites as catalysts for commercial applications.

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