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Article

Synthesis of Kaolinite Nanotubes as Heterogeneous Catalysts for Transesterification Reaction of Waste Cooking Oil into Biodiesel

Article Info

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Abstract. Kaolinite, a naturally abundant clay mineral, possesses a significant surface area and catalytic properties. To enhance its catalytic efficiency, modification into kaolinite nanotubes is necessary, as this transformation increases surface area and porosity. The synthesis of kaolinite nanotubes was achieved through a solvothermal method, incorporating multiple intercalation and rolling processes influenced by ultrasonic waves, subsequently utilizing these nanotubes as heterogeneous catalysts. The resulting kaolinite nanotube catalysts exhibited well-defined nanotube morphology and were applied in the transesterification of waste cooking oil, with variations in methanol-to-oil ratios. The optimal biodiesel yield achieved was 49.84%, obtained after a 3-hour reaction period using a 3% w catalyst at 60 °C, with a methanol-oil ratio of 3:1. This research highlights the potential of kaolinite nanotubes as effective catalysts in biodiesel production.

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1. Introduction

Energy consumption from fossil fuels is increasing rapidly due to population growth, transportation needs, and industry [1]. It is estimated that global energy demand will increase by 50% by 2040, potentially causing energy resource shortages and negative impacts on the environment [2]. According to the 2017 Indonesian Energy Outlook report from BPPT, in 2030 Indonesia is estimated to experience an oil import deficit of 540 million barrels per year. The use of fossil fuels is also a major cause of increasing greenhouse gas emissions, which contribute to global warming [3-6]. As fossil reserves dwindle and environmental pollution increases, researchers are looking for alternative energy sources [7]. One of the promising ones is biodiesel, which is renewable, biodegradable, and produces lower emissions than fossil fuels [8-9].

The main raw materials for biodiesel are vegetable oils, such as palm oil, soybean oil, and sunflower oil [10]. However, the use of vegetable oils can cause food problems and high production costs [1]. As a solution, cooking oil can be used because it is cheaper and helps reduce pollution. Disposal of waste cooking oil can create environmental problems, so processing it into biodiesel is a good option [11]. Biodiesel can be produced by various methods, such as oil blending, microemulsion, pyrolysis, and transesterification reactions [12-13]. Among all the methods, transesterification is the most popular because it is easy and efficient [11],[14]. This process involves the reaction of triglycerides from vegetable oils, animal fats, or waste cooking oils with short-chain alcohols such as methanol and ethanol, using a catalyst [15].

Common catalysts used to assist transesterification reactions are homogeneous and heterogeneous catalysts [16-17]. Homogeneous catalysts have better catalytic activity, but their use causes many problems, such as difficulty separating the catalyst from the product, soap formation, and corrosiveness [18-19]. Therefore, the use of heterogeneous catalysts is more recommended because they have low fabrication costs, easy separation of the catalyst from the product, high thermal stability, high recyclability, and low corrosion properties [18],[20]. Clay is an adsorbent material that can be used as a catalyst because it has a large surface a[rea, is porous, has high catalytic reactivity, has high ion exchange capacity, and is cheap [21-22]. One type of clay is kaolinite, which is abundant in nature and is cheaper than other types of clay [21], [23]. In previous research conducted by Rahayu et al. (2024), it was proven that thermally modified kaolinite has the potential to convert fatty acids in waste cooking oil, which can convert palmitic acid by 42% [24]. This discovery has the potential to serve as a catalyst in the production of biodiesel. In order to increase catalytic activity, it is necessary to modify the structure of kaolinite to increase its active side [25].

The use of materials with nanotube structures is recommended in the development of advanced materials. With this structure, the material can achieve a large surface area, high reactivity properties, and excellent catalytic activity. Kaolinite nanotubes in recent studies have been shown to be a new and effective adsorbent material that has a very large surface area, very high surface reactivity, excellent catalytic activity, and is porous[26-28]. The manufacture of kaolinite nanotubes is carried out through several stages of intercalation and electromagnetic wave induction[18]. The use of kaolinite nanotubes as a catalyst has never been done before. Therefore, this study focuses on exploring the potential of kaolinite nanotubes as a catalyst in the transesterification reaction of waste cooking oil which is expected to produce high biodiesel yields and good product selectivity.

2. Experimental Section
2.1. Materials

The materials used for the preparation of the catalyst were pure kaolinite obtained from Klinner Kimia. The materials used for the synthesis of kaolinite nanotubes were dimethyl sulfoxide (DMSO) of Merck brand, distilled water, methanol (CH_3OH) of Merck brand, nitric acid (HNO_3) of Merck brand, cetyl trimethyl ammonium bromide (CTAB) of Himedia brand, and ethanol (CH_3CH_2OH) of

Merck brand. The materials used for the transesterification reaction were methanol (CH_3OH) of Merck brand and waste cooking oil obtained from household cooking oil.

2.2. Synthesis of Kaolinite Nanotubes

Synthesis of kaolinite nanotubes was carried out in several stages of intercalation and electromagnetic wave induction. The first is intercalation with DMSO, 5 grams of kaolinite was dispersed into 50 mL of DMSO solution for 50 minutes at a temperature of 75ºC. Then the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 50 minutes at a temperature of 90ºC. After that, it was centrifuged for 5 minutes to separate the kaolinite intercalated with DMSO from the mixed solution and dried in an oven for 3 days at a temperature of 60ºC. The second is intercalation with methanol, 50 mL of methanol and 7 mL of HNO_3 p.a were mixed until homogeneous to form a methanol/HNO_3 solution. Then 2 grams of kaolinite-DMSO were dispersed in a methanol/HNO_3 solution with a magnetic stirrer for 50 minutes at a temperature of 75ºC. After that, the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 50 minutes at 90ºC. Then centrifuged for 5 minutes to separate the methanol-intercalated kaolinite from the mixed solution. After that, it was continued by washing with 50 mL which was stirred for 30 seconds and centrifuged again.

The washing process was carried out 5 times. Then the methanol-intercalated kaolinite was air-dried for 24 hours. The third was intercalation with CTAB, 2 grams of kaolinite-methanol were dispersed into 100 mL of CTAB solution for 50 minutes at 80ºC. Then the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 24 hours at 90ºC. After that, centrifuged for 5 minutes to separate the CTAB-intercalated kaolinite from the mixed solution and air-dried for 24 hours. Finally, 2 grams of kaolinite-CTAB were dispersed with 200 mL of ethanol after induction with electromagnetic waves. Then the mixture solution was sonicated for 90 minutes with a power of 150 W. After that, the mixture solution was centrifuged to separate the kaolinite nanotubes from the mixture solution. Then continued with washing with 50 mL of ethanol which was stirred for 30 seconds and centrifuged again. The washing process was carried out 8 times. Finally, the kaolinite nanotubes were dried in an oven for 2 days at a temperature of 80ºC. The kaolinite nanotubes were labeled KNT and then continued with characterization.

2.3. Transesterification of Waste Cooking Oil with The Help of Kaolinite Nanotube Catalyst

The transesterification reaction was carried out with the following procedure: for the reaction stoichiometry, the molar ratio of used cooking methanol and oil was varied to 3:1, 6:1, and 9:1, then the amount of catalyst used was 3% w/v to the waste cooking oil. First, the catalyst and methanol were heated to 50ºC with continuous stirring for 10-30 minutes. Next, 30 mL of purified waste cooking oil was added to a three-necked flask that had been previously heated at 105ºC until no more water bubbles remained, then the temperature was allowed to drop to 50ºC. Then mix the catalyst, methanol and purified waste cooking oil.

The transesterification reaction was carried out for 3 hours at 60ºC with a stirring speed of 700 rpm. At the end of the reaction, the flask was cooled to room temperature and the catalyst was separated from the product mixture using filter paper. The biodiesel product was separated from the glycerol using a separating funnel. Biodiesel is washed with hot distilled water (50ºC) with a volume of 1:1 and slowly homogenized until a white liquid is formed. The mixture is left to stand so that water collects at the bottom. Biodiesel is heated at a temperature above the boiling point of water (105ºC) until there are no more water bubbles.

2.4. Characterization

X-Ray Fluorescence (XRF) was used to identify the composition of compounds and elements in pure kaolinite and kaolinite nanotubes. X-Ray Diffraction (XRD) was used to see the success of intercalation compounds inserting into the kaolinite interlayers. Scanning Electron Microscopy (SEM) was used to observe the morphology of kaolinite and kaolinite nanotubes after coating the studied samples with a thin layer of gold. Structural-functional groups were identified using a Fourier Transform Infrared (FTIR) spectrometer. Gas Chromatography-Mass Spectrometry (GC-MS) was used to see the compound content in the biodiesel produced.
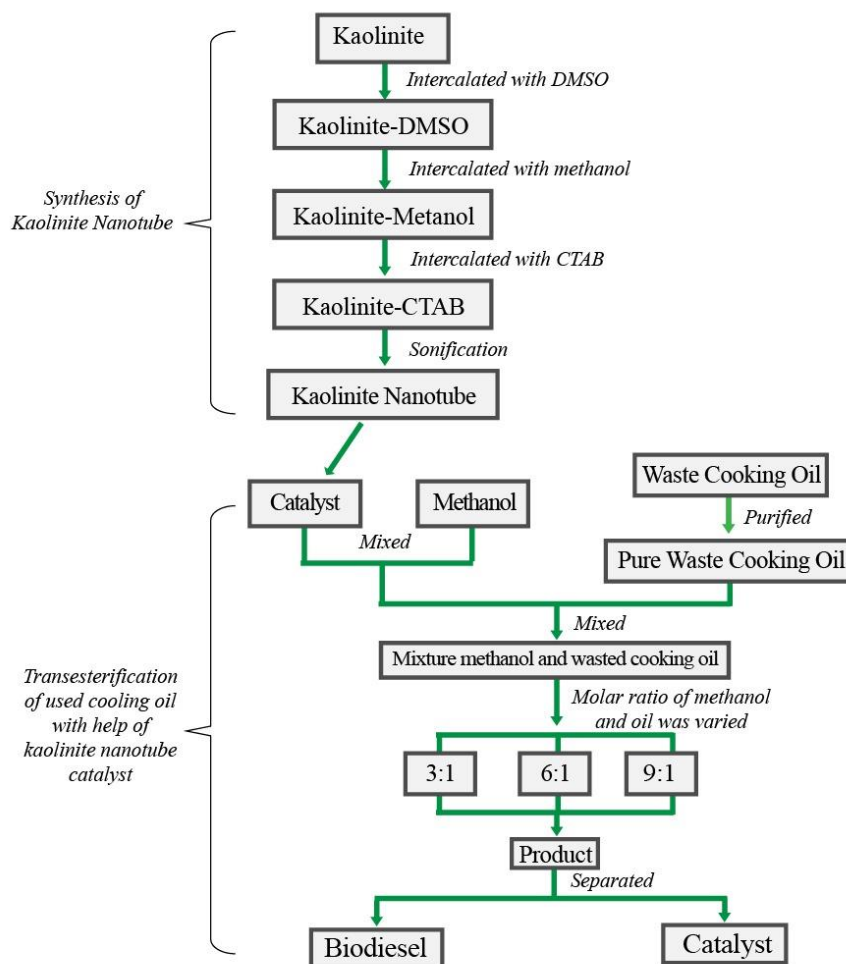

Figure 1. Procedure of experiment

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. XRF Analysis of Kaolinite and Kaolinite Nanotubes

The theoretical composition of pure kaolinite consists of 46.54% SiO_2, 39.5% Al_2O_3, and 13.96% H_2O, with an ideal Si:Al molar ratio of 1[29]. The results of the XRF analysis of kaolinite samples hereinafter referred to as Kaolinite (KI) and Kaolinite Nanotube (KN) are presented in Table 1. The results of the analysis show that KI has a Si molar ratio of 1.38, indicating that this sample belongs to the kaolinite clay mineral group. In addition, KI also contains other elements such as P, Fe, K, Ti,

Ca, and Ag. Meanwhile, the analysis of the KN sample showed an increase in the Si molar ratio to 1.46. This increase was due to a greater decrease in alumina content compared to silica in KN. In addition, the KN sample also contains sulfur of around 7.54%, which indicates the presence of DMSO molecules between the kaolinite layers, as well as a Br content of 1.87%, which indicates the presence of CTAB molecules and Br- ions bound to kaolinite cations.

Table 1. Chemical elemental composition of kaolinite and kaolinite nanotube samples

	SiO_2	Al_2O_3	P_2O_5	F_e2O_3	K_2O	TiO_2	CaO	Ag_2O	SO_3	Br	$n_{(Si)}/n_{(Al)}$
Kaolinite	56.71	34.67	3.48	1.84	1.35	0.71	0.63	0.23	0	0	1.38
Kaolinite Nanotube	52.13	30.29	3.24	1.83	1.35	0.73	0.73	0.11	7.54	1.87	1.46

3.1.2. XRD Analysis of Kaolinite (KI)

X-ray diffraction (XRD) analysis was used to evaluate the phase composition, crystal structure, and structural changes that occur during the intercalation process[29]. The XRD test results showed a spectrum pattern that matched kaolinite, namely JCPDS 01-089-6538. The XRD curve for KI shown in Figure shows an ideal crystal structure, characterized by sharp peaks at 7.16 Å at a 2θ angle of 12.35° and 3.58 Å at a 2θ angle of 24.85° for $d_{(001)}$ and $d_{(002)}$. In addition, eleven other diffraction peaks that are clearly visible, including $d_{(020)} = 4.47$ Å, $d_{(\bar{1}10)} = 4.36$ Å, $d_{(\bar{1}\bar{1}1)} = 4.19$ Å, $d_{(0\bar{2}1)} = 3.87$ Å, $d_{(111)} = 3.34$ Å, $d_{(\bar{2}01)} = 2.57$ Å, $d_{(\bar{1}\bar{3}1)} = 2.53$ Å, $d_{(200)} = 2.49$ Å, $d_{(003)} = 2.38$ Å, $d_{(\bar{2}02)} = 2.34$ Å, dan $d_{(131)} = 2.29$ Å. The crystallinity degree of KI was recorded at 0.94, indicating a high level of crystallinity. From the comparison of XRD curves, the kaolinite sample shows a spectrum pattern similar to triclinic kaolinite. The results of XRD analysis on KI prove that the sample used is kaolinite in triclinic form.
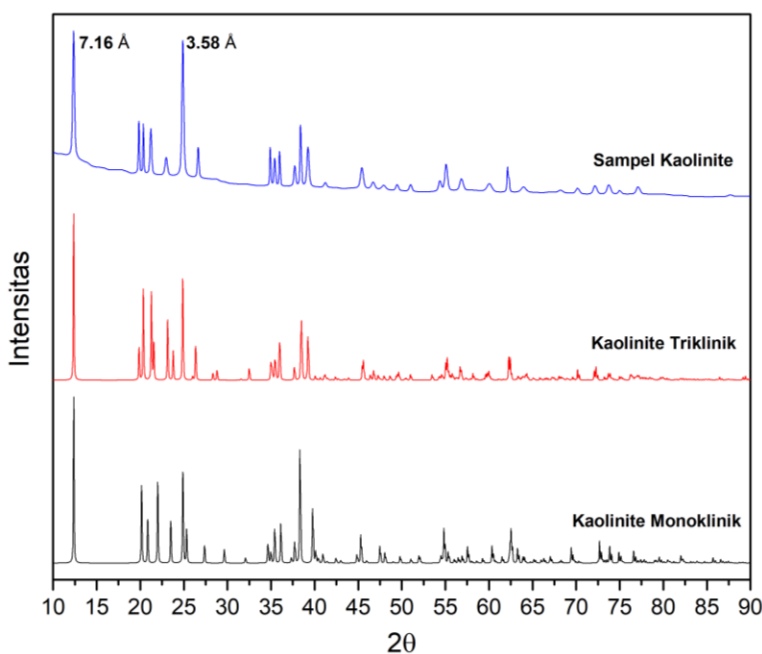

Figure 2. XRD test results of kaolinite

3.1.3. XRD Analysis of Intercalated Compounds and Kaolinite Nanotubes (KN)

KI cannot be directly converted into KN because the bonds between layers in kaolinite sheets are very strong. Therefore, the formation of intercalation compounds is needed to facilitate the separation of the stacked layers. Intercalation compounds such as Kaolinite-DMSO (KD), Kaolinite-Methanol (KM), and Kaolinite-CTAB (KC) are made to break the bonds between kaolinite layers. XRD analysis was performed on the intercalation compounds to evaluate the success of the intercalation process between kaolinite layers.

Kaolinite is difficult to intercalate due to the strong hydrogen bonds between its layers. Small and highly polar molecules, such as dimethyl sulfoxide (DMSO), are the right choice to break the hydrogen bonds. The XRD results for KD can be seen in Figure . The analysis shows that there is a shift in the diffraction peak from a 2θ angle of 12.35º to 7.87º, which results in an increase in the basal distance of the $d_{(001)}$ diffraction peak by 4.06 Å, from 7.16 Å to 11.22 Å after the intercalation of dimethyl sulfoxide molecules between kaolinite layers. This indicates that the intercalation of DMSO into the kaolinite layer was successful. The sharp shape of the $d_{(001)}$ diffraction peak indicates that the dimethyl sulfoxide molecules are highly oriented in the kaolinite layer. Furthermore, several other diffraction peaks in kaolinite decrease or even disappear, indicating that the degree of crystallinity of kaolinite decreases.
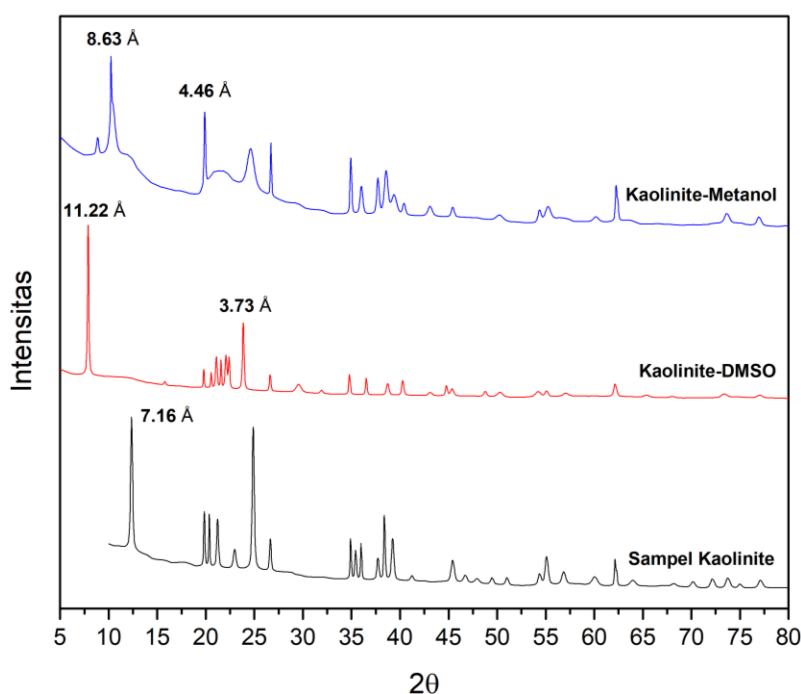

Figure 3. XRD Results of Kaolinite, Kaolinite-DMSO, and Kaolinite-Methanol

Furthermore, intercalation of kaolinite with methanol, which is a non-polar molecule, is carried out to replace the small polar dimethyl sulfoxide (DMSO) molecule. KM is used as an intermediary agent to insert macromolecular intercalating agents such as cetrimonium bromide (CTAB), resulting in KC. The XRD results for KM can be seen in Figure 3. The analysis shows a shift in the diffraction peak from an angle of 2θ 7.87º to 10.23º, resulting in a decrease in the basal distance by 2.59 Å, from 11.22 Å to 8.63 Å. This indicates that the intercalation of methanol molecules into the kaolinite layer was successful. However, a new peak appears at an angle of 2θ 8.86˚, indicating that there are still DMSO molecules remaining between the kaolinite layers.

Finally, the synthesis of KC to produce a very wide basal distance between kaolinite layers. This allows the surface to peel off into individual kaolinite sheets when induced by ultrasonic waves, which were roll the kaolinite sheets into KN. The success of KC synthesis is indicated by the appearance of a diffraction peak at an angle of 2θ 2.30° [29], while the success of KN synthesis is seen from the slope of the 2θ angle between 1°- 4° [30]. However, due to the limitations of the XRD instrument that can measure the diffraction pattern from an angle of 2θ 2°, XRD analysis for KC and KN has not been carried out.

3.1.4. SEM Analysis of Kaolinite (KI) and Kaolinite Nanotubes (KN)

SEM analysis is used to characterize the surface morphology of minerals and the changes that occur in them [29]. In this study, SEM was applied to observe the transformation of KI into KN. The results of the SEM test on KI can be seen in Figure , which shows that KI has a highly crystalline flake shape and a pseudo-hexagonal structure. The KI flakes are stacked, forming a stack of kaolinite sheets. Figure shows the SEM scan results of KN. After the intercalation process and ultrasonic wave induction, the stack of kaolinite sheets was successfully broken into individual sheets, which then rolled into a tube structure. This image indicates the successful formation of KN, and this result can replace XRD analysis for KC and KN which cannot be done.
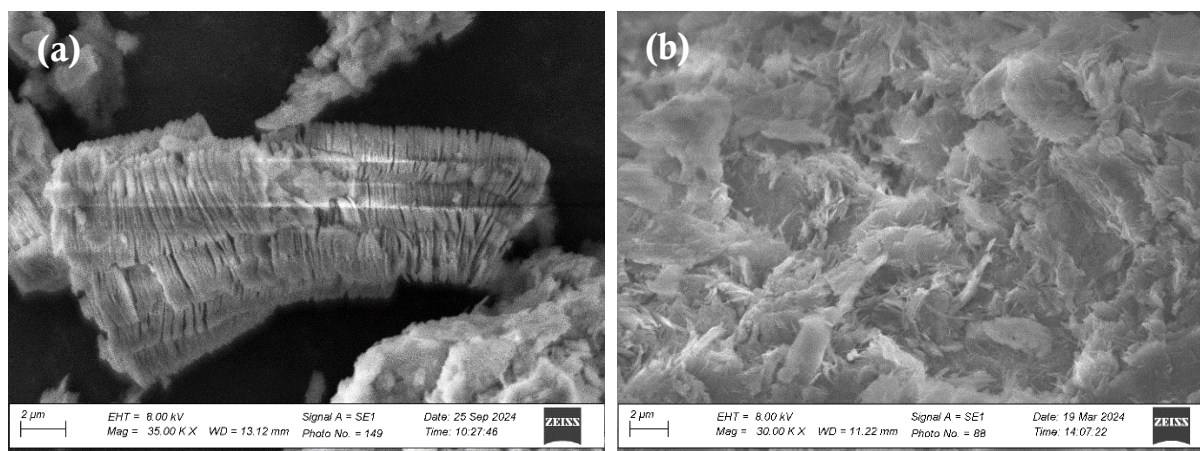

Figure 4. SEM results of (a) Kaolinite (KI) and (b) Kaolinite Nanotubes (KN)

3.2. Catalytic Activity Test of Kaolinite (KI) and Kaolinite Nanotube (KN) Catalysts

Catalyst activity test in this study was conducted on the transesterification reaction of waste cooking oil into biodiesel. The catalysts used in this reaction were KI and KN, each of which was reacted with variations in the ratio of methanol and oil of 3:1, 6:1, and 9:1. The transesterification reaction was carried out at a temperature of 60°C, with a stirring speed of 700 rpm, and a reaction time of 3 hours.

The biodiesel yield produced by the KI catalyst can be seen in Figure . Based on the biodiesel yield results obtained, the biodiesel yield increased from the molar ratio reaction of methanol and oil 3:1 to 6:1 and decreased at a ratio of 9:1. The optimum biodiesel yield was obtained at a variation of the molar ratio of methanol:oil 6:1, which was 12,02% and the minimum at a molar ratio of methanol:oil 9:1, which was 0,34%. In the transesterification reaction, the use of excess methanol is useful for encouraging the formation of methyl esters, where the transesterification reaction is reversible so that it plays an important role in the formation of biodiesel.

At a molar ratio of 6:1 to 9:1 there was a decrease, this is estimated because the use of excessive methanol or beyond the ideal limit can reduce the concentration of triglycerides, so that the interaction between triglyceride molecules and methoxide ions becomes limited and not optimal. This reduces the rate of reaction of ester compound formation. In addition, excessive methanol can dissolve

glycerol, complicate separation, and contribute to the re-formation of triglycerides, leading to a reversible reaction and reducing the formation of ester compounds. Excess methanol at the active site of the catalyst also reduces the interaction between reactants and can cause deactivation of the active site on the catalyst [18],[31].
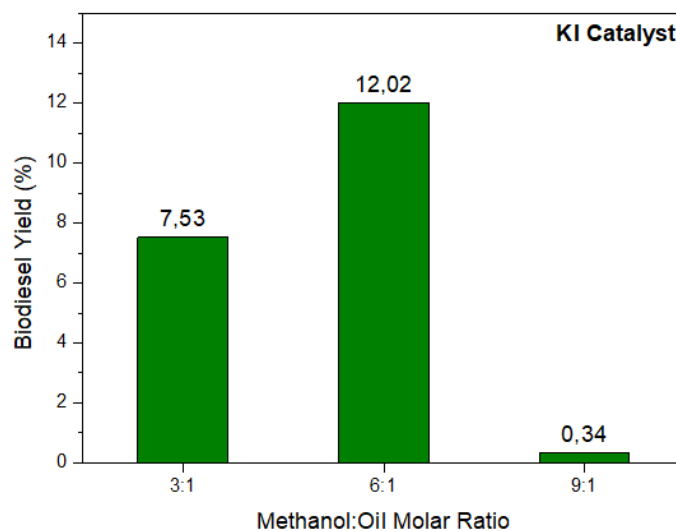

Figure 5. Biodiesel yield produced by KI catalyst

The FAME content produced from the transesterification reaction using KI catalyst can be seen in Table 2. In the reaction with a methanol:oil ratio of 3:1 the most dominant type of FAME is 9-Octadecenoic acid, methyl ester, (E)-. Then, at a methanol:oil ratio of 9:1, the types of FAME produced are 9-Octadecenoic acid (Z)-, methyl ester and Pentadecanoic acid, 14-methyl-, methyl ester in equal amounts. Meanwhile, in the reaction with a methanol:oil ratio of 6:1, in addition to the formation of methyl ester, ethyl ester is also produced, which is included in the biodiesel category. The ethyl ester produced at this ratio is Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester.

Table 2. %FAME dan %FAE content produced with KI catalyst

No	FAME/FAE	Carbon Chain	%Area Fame/Fae Katalis KI		
			3:1	6:1	9:1
1	Hexadecanoic acid, methyl ester	C16	0.45	0.9	
2	9-Octadecenoic acid (Z)-, methyl ester	C18	10.71		0.28
3	Pentadecanoic acid, 14-methyl-, methyl ester	C15			0.28
4	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	C16		22.78	

The biodiesel yield produced by the KN catalyst can be seen in Figure . The analysis results show that the biodiesel yield decreases with increasing molar ratio of methanol and oil. The maximum biodiesel yield was obtained at an oil molar ratio of 3:1, which was 49.84%, while the minimum yield was recorded at a ratio of 9:1, with a value of 32.67%. This decrease is thought to occur for the same reason as that which occurs in the biodiesel yield when using kaolinite catalyst.

The conversion of KI to KN increases the surface area of kaolinite, which in turn increases the adsorption capacity and the number of active sites of kaolinite as a catalyst. With the increase in adsorption capacity, more methanol and triglycerides can be adsorbed on the kaolinite surface, thus triggering the transesterification reaction. In addition, the increase in the number of active sites allows more methanol to be converted into methoxy ions, which can react with triglycerides that are also adsorbed on the kaolinite surface. The presence of cations in KN, such as Fe^{2+}, K^+, Ti^{2+}, Ca^{2+}, and Ag^+, with percentages of 1.83%, 1.35%, 0.73%, 0.73%, and 0.11%, respectively, increases the active sites of KN. In addition, the presence of Br^- anions of 1.87% also contributes to the increase in the active sites of KN as a catalyst. This is proven by the increase in biodiesel yield from using the KN catalyst compared to using the KI catalyst.
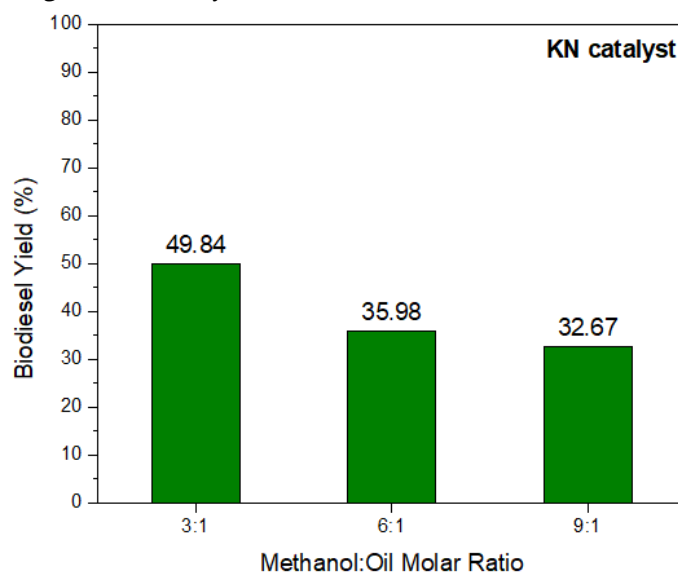

Figure 6. Biodiesel yield produced by KN catalyst

The content of FAME produced from the transesterification reaction using KN catalyst can be seen in Table 3. The increasing ratio of methanol:oil, the selectivity of FAME increases. In the reaction with a methanol:oil ratio of 3:1 and 6:1, the most dominant types of FAME are Hexadecanoic acid, methyl ester and 9-Octadecenoic acid, methyl ester, (E)-. Then with the increase in the methanol:oil ratio from 3:1 to 6:1 shows that the selectivity of FAME increases from 6 types to 4 types of FAME. While in the reaction with a methanol:oil ratio of 9:1 produces very selective FAME, which only produces Hexadecanoic acid, methyl ester.

Table 3. %FAME content produced with KN catalyst

No	FAME	Carbon Chain	%Area Fame Katalis KN		
			3:1	6:1	9:1
1	Dodecanoic acid, methyl ester	C12	0.21	0.32	
2	Hexadecanoic acid, methyl ester	C16	19.05	21.37	52.42
3	6-Octadecenoic acid, methyl ester	C18		0.66	
4	9-Octadecenoic acid (Z)-, methyl ester	C18	2.42		
5	9-Octadecenoic acid, methyl ester, (E)-	C18	28.93	32.82	
6	Nonadecanoic acid, methyl ester	C19	17.81		
7	Docosanoic acid, methyl ester	C22	3.41		

4. Conclusion

Kaolinite nanotubes were successfully synthesized from kaolinite and used as heterogeneous acid catalysts. This catalyst was applied in the transesterification of waste cooking oil. Kaolinite nanotubes (KN) achieved a biodiesel yield of 49.84% after a 3-hour reaction interval using 3%w catalyst in the presence of a methanol-oil ratio of 3:1 at a reaction temperature of 60˚C. Kaolinite was shown to increase the surface area and catalytic activity compared to kaolinite.

5. Acknowledgement

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