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Article

Kaolinite Nanotubes as Support Catalysts of Sulfuric Acid (H_2SO_4) for Transesterification Reaction of Waste Cooking Oil into Methyl Ester for Biodiesel

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Abstract. Clay is one of the non-biological natural materials composed of various types of minerals, with kaolinite as one of the most abundant components. Kaolinite is not only available in nature but also has a relatively low production cost compared to other minerals, making it an attractive raw material for various applications, including catalytic reactions. However, the natural catalytic properties of kaolinite are still limited. This study aims to improve the catalytic performance of kaolinite by converting it into kaolinite nanotubes and utilizing it as a support for sulfuric acid catalysts. Analysis using XRD and TEM revealed that the kaolinite crystal phase remained stable after being modified with sulfuric acid, while kaolinite nanotubes underwent little structural change. In addition, characterization via FTIR and XRF confirmed the presence of sulfate ions in kaolinite nanotubes and kaolinite after combination with sulfuric acid. Catalytic test on transesterification of used cooking oil under uniform conditions (catalyst 3% w/v, oil to methanol ratio 1:6, temperature 90 °C, and stirring speed 700 rpm) showed that sulfuric acid supported by kaolinite nanotubes gave the best performance, producing methyl ester of 65.01%. These findings indicate that converting kaolinite into nanotubes significantly improves its performance as a catalyst support. Practically, this increase in catalytic activity contributes to the efficiency of used cooking oil-based biodiesel production, which can reduce dependence on virgin vegetable oil raw materials and support waste oil recycling efforts. In addition, the use of cheap and easily available kaolinite-based catalysts can reduce the cost of biodiesel production, making it more competitive as an environmentally friendly fuel.

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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 area, 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]. However, kaolinite has a small surface area so that its potential as a catalyst is still limited, therefore it is necessary to modify the structure of kaolinite to expand its surface area so that it can increase its catalytic activity. 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].

Modification of kaolinite is carried out by converting kaolinite into kaolinite nanotubes to enhance its surface area and catalytic activity [15]. The synthesis of kaolinite nanotubes involves several intercalation stages [12], followed by the exfoliation of layers into kaolinite sheets, which then roll under the influence of ultrasonic waves into kaolinite nanotubes [17],[28]. Previous studies have shown that modifying kaolinite into kaolinite nanotubes can significantly improve its catalytic activity in transesterification reactions. In Abukhadra's study, the use of kaolinite nanotubes as a catalyst was investigated by doping potassium into the kaolinite nanotubes (K+/KNT) for the transesterification of waste cooking oil, yielding a biodiesel conversion of 98% [18]. However, research on the utilization of kaolinite nanotubes as an H_2SO_4 catalyst support in the transesterification of waste cooking oil for biodiesel production has not yet been conducted.

Therefore, to find an alternative for efficient, environmentally friendly, and sustainable biodiesel production from used cooking oil, this study focuses on exploring the potential of kaolinite nanotubes as a catalyst support for H_2SO_4. The synthesis of kaolinite nanotubes was carried out using the solvothermal method, which involves several stages of intercalation and rolling influenced by ultrasonic waves. Practically, this study is expected to contribute to the development of biodiesel by increasing the efficiency of the catalyst in the transesterification reaction, thereby reducing the amount of catalyst needed and accelerating the conversion process of used cooking oil into biodiesel. In addition, the use of kaolinite nanotubes as a catalyst support for H_2SO_4 can provide a more environmentally friendly solution because it reduces the use of homogeneous catalysts that are difficult to separate and have the potential to pollute the environment. With the increasing effectiveness of heterogeneous catalysts based on kaolinite nanotubes, the cost of biodiesel production can also be reduced, making it more economical and competitive in the alternative fuel market.

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 75°C. Then the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 50 minutes at a temperature of 90°C. 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 60°C. 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 75°C. After that, the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 50 minutes at 90°C. 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 80°C. Then the mixed solution was transferred into a hydrothermal reactor and heated in an oven for 24 hours at 90°C. 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. Kaolinite as an Acid Catalyst Support (H_2SO_4)

In this process, 5 grams of KI were dispersed in 12.5 mL of H2SO4 (50%) using a reflux method for 3 hours at a temperature of 90°C with a stirring speed of 500 rpm. The sample was then allowed to cool to room temperature. Subsequently, the sample was dried in an oven at 110°C for 8 hours. The sample was named KI-H2SO4, ground into a fine powder, and subjected to XRF and FTIR characterization tests.

2.4. Kaolinite Nanotube as an Acid Catalyst Support (H_2SO_4)

In this process, 5 grams of KNT were dispersed in 12.5 mL of H2SO4 (50%) using a reflux method for 3 hours at a temperature of 90°C with a stirring speed of 500 rpm. The sample was then allowed to cool to room temperature. Subsequently, the sample was dried in an oven at 110°C for 8 hours. The sample was named KNT-H_2SO_4, ground into a fine powder, and subjected to XRF and FTIR characterization tests.

2.5. Transesterification of Waste Cooking Oil

The transesterification reaction was carried out with the following procedure: for the reaction stoichiometry, the molar ratio of methanol and used cooking oil was varied to 3:1, 6:1, and 9:1, then the amount of catalyst used was 3% w/v to the used cooking oil. The selection of this molar ratio is based on the Le Chatelier principle, where increasing the amount of methanol is expected to shift the reaction equilibrium towards the product and increase the conversion of biodiesel. However, a ratio that is too high can increase the cost of separating excess methanol at the purification stage.

First, the catalyst and methanol were heated to a temperature of 50ºC with continuous stirring for 10-30 minutes. This heating process aims to ensure that the catalyst is evenly dispersed in methanol before being mixed with used cooking oil, thereby increasing reaction efficiency. Next, 30 mL of pure used cooking oil was put into a three-necked flask that had previously been heated at a temperature of 105ºC until there were no more water bubbles. This heating is done to remove water in the used cooking oil which can cause soap formation during the transesterification reaction. After that, the oil temperature is allowed to drop to 50ºC to avoid evaporation of methanol when mixing with the catalyst. Then, the mixture of catalyst, methanol, and pure used cooking oil is stirred at a speed of 700 rpm for 3 hours at a temperature of 60ºC.

The selection of a temperature of 60ºC is based on the boiling point of methanol (64.7ºC) so that the reaction takes place optimally without causing excessive evaporation. The reaction time of 3 hours was chosen based on the results of previous studies which showed that within that time span, biodiesel conversion can reach its optimum point before product degradation or unwanted side reactions occur. At the end of the reaction, the flask is cooled to room temperature, then the catalyst is separated from the product mixture using filter paper.

The biodiesel product is separated from the glycerol using a separating funnel, where the glycerol which has a higher density will settle at the bottom. After separation, the biodiesel is washed with hot distilled water (50ºC) with a volume of 1:1 and slowly homogenized until a white liquid is formed, indicating the presence of catalyst and soap residues in the biodiesel. The mixture is left to stand until water collects at the bottom, then the biodiesel is heated at a temperature above the boiling point of water (105ºC) until there are no more water bubbles. This heating process aims to remove residual water and methanol still contained in the biodiesel, thereby increasing the purity and stability of the final product. An explanation of the selection of these operating conditions is important to ensure the efficiency of the reaction and the quality of the biodiesel produced, while the details of the separation and purification process of biodiesel help in understanding the final stages of production that affect the characteristics of the fuel produced.

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. Transmission Electron Microscopy (TEM) 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.

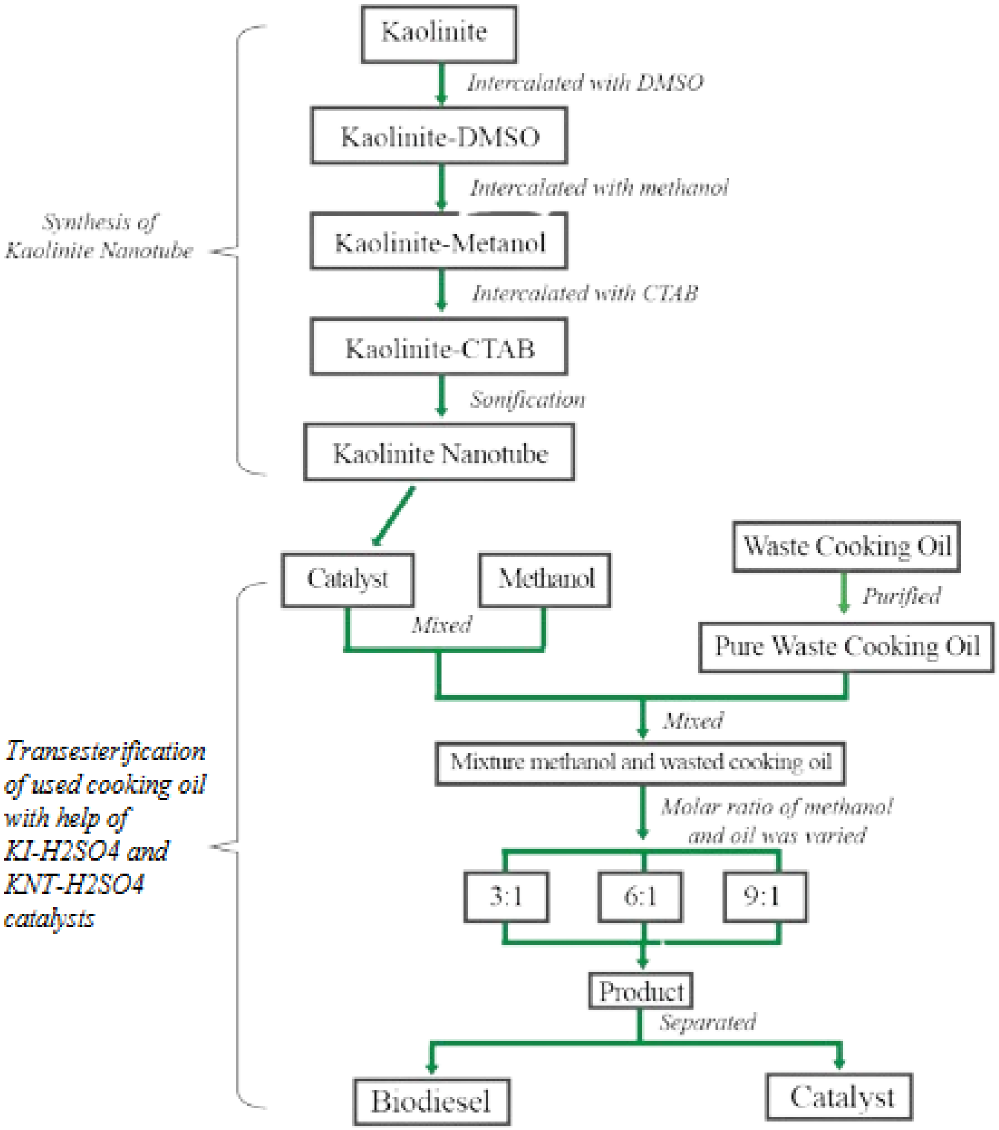

Figure 1. Work procedures

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. XRF Analysis of KI-H_2SO_4 and KNT-H_2SO_4

Chemical composition analysis was conducted to understand the changes in composition occurring in the sulfuric acid-supported parent kaolinite (KI-H_2SO_4), and sulfuric acid-supported kaolinite nanotube (KNT-H_2SO_4). 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]. Chemical composition analysis was conducted to understand the changes in composition occurring in the parent kaolinite (KI), sulfuric acid-supported parent kaolinite (KI-H_2SO_4), and sulfuric acid-supported kaolinite nanotube (KNT-H_2SO_4). Understanding the chemical composition is essential to assess the success of structural modification into nanotubes and the treatment with sulfuric acid. The characterization method used was X-Ray Fluorescence (XRF) [56-57], which provides quantitative information on the sample's content. The XRF test results for KI-H_2SO_4 and KNT-H_2SO_4 samples are presented in Table 1.

Table 1. Chemical Element Composition of KI, KI-H_2SO_4, and KNT-H_2SO_4

	SiO_2	Al_2O_3	P_2O_5	Fe_2O_3	K_2O	TiO_2	CaO	Ag_2O	SO_3	$n_{(Si)}/n_{(Al)}$
KI-H_2SO_4	56.27	34.77	3.30	1.79	1.46	0.25	0.53	0	1.48	1.36
KNT-H_2SO_4	51.20	33.47	3.44	1.81	1.33	0.74	0.62	0	5.90	1.28

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 process[29]. The crystal phase composition and crystal structure of KI-H_2SO_4 and KNT-H_2SO_4 were obtained from XRD analysis data. The diffractogram of KI, taken from previous research [24], indicates that KI has a triclinic crystal phase. The XRD diffractograms of KI-H_2SO_4 and KNT-H_2SO_4 are shown in Figure 2. The XRD diffractogram of KI-H_2SO_4 exhibits a spectrum pattern matching the standard kaolinite spectrum with a triclinic crystal phase, demonstrating that the kaolinite structure remains intact after impregnation with H_2SO_4. However, a slight increase in peak intensity at the 2θ angle of 26.6° suggests a combination of kaolinite and H_2SO_4 peaks, indicating that sulfuric acid adheres to the kaolinite surface.

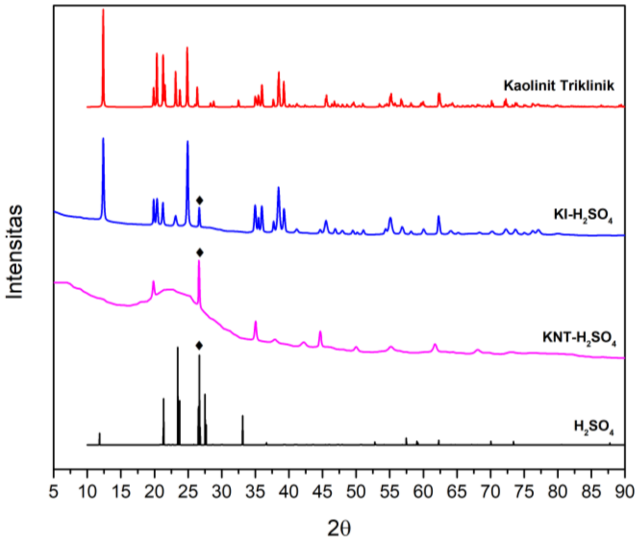

Figure 2. XRD test results of KI-H_2SO_4 and KNT-H_2SO_4

In the KNT-H_2SO_4 diffractogram, the successful synthesis of KNT can be identified by the tilting of the diffractogram at a 2θ angle of approximately 1° [30]. However, due to the XRD instrument limitations, which can only measure angles starting from 2θ 5°, the continuation of this tilt beyond 2θ 5° was observed, confirming the successful formation of the kaolinite nanotube structure. Additionally, the decrease or even disappearance of kaolinite peaks indicates a reduction in kaolinite crystallinity, further supporting the formation of kaolinite nanotubes. The presence of sulfuric acid adhered to the KNT surface is evidenced by a significant increase in the peak intensity at 2θ 26.5°. This indicates a combination of kaolinite and H_2SO_4 peaks, showing an increased amount of sulfuric acid adhering to the surface of kaolinite modified into nanotubes compared to kaolinite before modification.

The change of crystal structure from kaolinite to kaolinite nanotubes significantly affected the catalytic performance of this material. The reduction of crystallinity in KNT-H_2SO_4 indicated that the structural modification led to an increase in the specific surface area and the number of available catalytic active sites. The nanotube structure allowed a more even dispersion of sulfuric acid, which improved the interaction between the catalyst and the substrate during the transesterification reaction. In addition, the transformation of kaolinite from a layered structure to nanotubes resulted in increased porosity and accessibility of active sites by reactant molecules.

In heterogeneous catalysis, surface area and accessibility of active sites play an important role in determining the reaction efficiency. The nanotube structure improved the diffusion of reactants into the catalyst, reduced mass barriers, and allowed a more effective interaction between waste cooking oil and the catalyst during transesterification. The presence of more sulfuric acid on the surface of kaolinite nanotubes compared to pure kaolinite also increased the acidity of the catalyst, which contributed to the acceleration of the transesterification reactions. This higher acidity helps in converting triglycerides to methyl esters more efficiently, thereby reducing the possibility of soap formation that can inhibit biodiesel conversion. Thus, the change in crystal structure from kaolinite to nanotubes not only increases the surface area and porosity but also strengthens the catalytic interaction through increased distribution of sulfuric acid and accessibility of active sites. This explains why KNT-H_2SO_4 showed better catalytic performance than KI-H_2SO_4 in the transesterification reaction of waste cooking oil.

3.1.4. TEM Analysis of KNT-H_2SO_4

Analysis using Transmission Electron Microscopy (TEM) was conducted to observe the internal structure and detailed morphology at the nanometer scale of KNT-H_2SO_4 [29]. This technique provides more in-depth information compared to SEM, particularly regarding the arrangement of the layer structure and morphological transformations occurring during the nanotube formation process. The TEM results for KNT-H2SO4 can be seen in Figure 3.

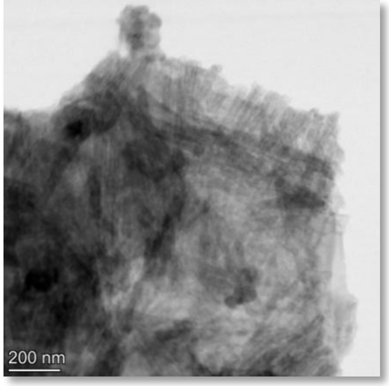

Figure 3. TEM results of KNT-H_2SO_4

After being modified with sulfuric acid, the kaolinite nanotube structure of KNT-H2SO4 remains visible, despite significant morphological changes. TEM images show increased agglomeration, evident from the dark areas in the TEM results. This indicates the distribution of sulfuric acid active groups on the nanotube surface. The modification adds layers or active groups to the surface of KNT, enhancing the catalytic properties of the material by increasing surface acidity. The sulfuric acid groups distributed on the nanotubes create effective active sites that support catalytic reactions, such as in transesterification reactions. Although this modification may cause partial damage to the regular tubular structure, these changes reflect the formation of a new, more reactive material. The increased surface acidity makes this material highly effective as a heterogeneous catalyst. The initially uniform structure of KNT with regular pores transforms into a material with more active sites. This transformation demonstrates that KNT as a sulfuric acid catalyst support is a highly promising material for various high-performance catalytic applications.

3.1.5. FTIR Analysis of KI-H2SO4 and KNT-H_2SO_4

Changes in functional groups and chemical bonds within the structure of kaolinite as a sulfuric acid support (KI-H_2SO_4) and kaolinite nanotubes as a sulfuric acid support (KNT-H_2SO_4) were analyzed using FTIR. The FTIR analysis results for KNT and KNT-H2SO4 can be seen in Figure 4.

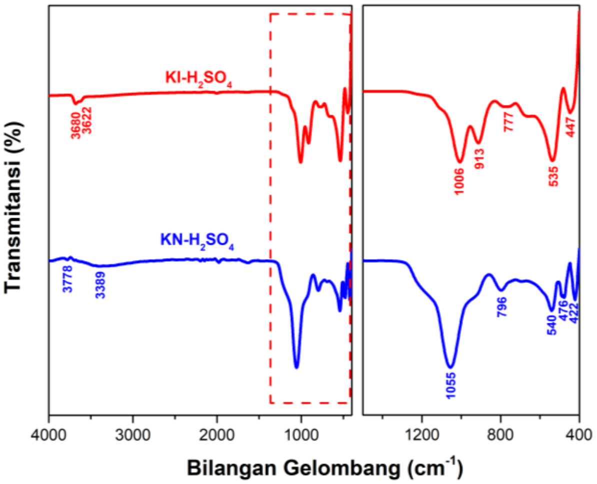

Figure 4. Spectra FTIR of KI- H2SO4 and KNT-H2SO4

The identification of absorption bands in KI-H2SO4 shows a range at 3680 cm^{-1}, indicating the presence of external O-H groups bonded to Si-OH [25-26]. The band at 3622 cm^{-1} corresponds to internal O-H groups arising from hydrogen bond vibrations between kaolinite layers. The band at 1006 cm^{-1} is associated with symmetric stretching of S=O in sulfonate groups (SO_3H). The band at 913 cm^{-1} represents the deformation of internal Al-OH groups, related to Al-OH stretching and bending vibrations. Meanwhile, two absorption bands at 535 cm^{-1} and 447 cm^{-1} indicate Si-O-Al bending vibrations [29]. In the spectrum of KNT-H2SO4, the observed absorption band at 1055 cm^{-1} indicates the presence of SO_3 stretching and O-S-O stretching in SO_3H [30].

This suggests that KNT has successfully served as an H_2SO_4 catalyst support for a heterogeneous acid catalyst. The absorption bands observed at 3389 and 3778 cm^{-1} correspond to the stretching vibrations of Al-OH molecules. The presence of Si-O from Si-O-Si bonds is observed at a wavelength of 796 cm^{-1}. Meanwhile, the range of 422-540 cm^{-1} indicates Si-O-Al bending vibrations [29]. The appearance of a new band at 476 cm^{-1} is associated with symmetric vibrations of the S–O group in sulfonate groups (SO_3H). This peak confirms the presence of SO_3H groups derived from sulfuric acid bonded to the kaolinite nanotubes.

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

A catalyst activity test in this study was conducted to evaluate the performance of the catalysts in the transesterification reaction of used cooking oil into biodiesel. The catalysts used were KI- H_2SO_4 and KNT-H_2SO_4, each tested with varying oil-to-methanol molar ratios of 1:3, 1:6, and 1:9. The transesterification reaction was carried out at a reaction temperature of 60ºC, a stirring speed of 700 rpm, and a reaction time of 3 hours.

The biodiesel yield produced by the KI- H_2SO_4 and KNT-H_2SO_4 catalyst is shown in Figure 5. Based on the results, the biodiesel yield at each variation of the oil:methanol molar ratio remained relatively stable. The highest biodiesel yield, 65.01%, was achieved at an oil:methanol ratio of 1:6, while the lowest yield, 61.69%, occurred at an oil:methanol ratio of 1:9. This indicates that using KNT as a support for the H_2SO_4 catalyst enhances its catalytic properties. The biodiesel yield results with the KNT-H_2SO_4 catalyst were nearly identical to those obtained using H_2SO_4 alone. However, the KNT-H_2SO_4 catalyst offers the advantage of being easily separated from the product and can be reused, making it a more efficient and sustainable option [18],[31].

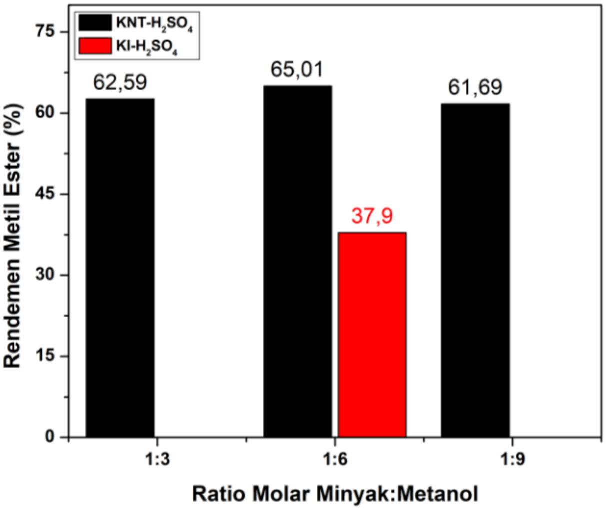

Figure 5. Catalytic performance of KI-H2SO4 and KNT-H2SO4 in the transesterification of waste cooking oil with a catalyst amount of 3% (w/v) relative to the waste cooking oil, at a temperature of 90°C and a stirring speed of 700 rpm.

Compared with other heterogeneous catalysts, such as CaO, ZnO, and K_2CO_3, this modified kaolinite-based catalyst shows competitive efficiency. CaO catalyst, for example, can produce higher biodiesel yield (>90%) [32], but has the disadvantage of catalyst degradation due to reaction with water and carbon dioxide, and the need for higher operating temperatures (>65ºC) to maintain its activity. ZnO and K_2CO_3 also have good activity, but often require initial activation or more extreme reaction conditions to achieve optimal efficiency [33]. Compared with zeolite and alumina-based catalysts that are also used as supports for acid catalysts, KNT-H_2SO_4 has advantages in terms of thermal stability and ease of synthesis. In addition, the modification of kaolinite into nanotubes increases the surface area and accessibility of active sites, which supports the improvement of catalytic efficiency.

From an economic perspective, this method has the potential to be cheaper than using homogeneous catalysts such as H_2SO_4 alone, because KNT-H_2SO_4 can be reused without the need for repeated neutralization and separation, which often increases the cost of biodiesel production [34]. In addition, kaolinite as the main raw material is abundantly available and has a much lower price than synthetic metal oxide or zeolite-based catalysts, making it an economical choice for large-scale biodiesel production. From a sustainability perspective, this method is more environmentally friendly than homogeneous catalysts because it reduces acid waste that must be neutralized. Easier catalyst separation also reduces water consumption in the biodiesel washing process, thereby reducing the environmental footprint of biodiesel production. In addition, the use of used cooking oil as a raw material helps reduce domestic and industrial waste, supporting the concept of a circular economy by reusing previously wasted resources. Overall, although the biodiesel yield produced by KNT-H_2SO_4 has not reached the levels obtained with some other heterogeneous catalysts, the advantages in economic efficiency, ease of separation, and lower environmental impact make it an attractive solution for sustainable biodiesel production.

4. Conclusion

This study successfully demonstrated that transforming kaolinite into nanotube form significantly enhances its catalytic properties. Parent kaolinite and kaolinite nanotubes were used as supports for sulfuric acid catalysts. XRD and TEM analyses revealed that the crystalline phase of kaolinite remained stable after combining with sulfuric acid, whereas similar treatment caused slight changes in the kaolinite nanotubes. Characterization using FTIR and XRF confirmed the presence of sulfate ions after the combination of kaolinite and kaolinite nanotubes with sulfuric acid. Catalytic tests on the transesterification of waste cooking oil, under identical operating conditions (3% catalyst w/v, oil-to-methanol ratio of 1:6, temperature of 90°C, and stirring speed of 700 rpm), showed that sulfuric acid supported by kaolinite nanotubes delivered the best results, achieving a methyl ester yield of 65.01%.

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