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Research Paper

# Preparation of KI/KIO$_3$/Methoxide Kaolin Catalyst and Performance Test of Catalysis in Biodiesel Production

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**Abstract**

Kaolin is a natural ingredient that is in abundance and has not been widely used. Kaolin is a source of silica ($SiO_2$) and alumina ($Al_2O_3$) so that it can be used as a heterogeneous catalyst in biodiesel production. This research aims to examine the influence of using impregnated kaolin as a heterogeneous catalyst on production of biodiesel. Research methods include calcination of natural kaolin, impregnation of kaolin using KI, KIO$_3$, and preparation of kaolin-methoxide in various concentrations, as well as biodiesel production using an impregnated kaolin catalyst. The catalyst was characterized using XRD and SEM. The catalyst was tested for basicity using the Hammet indicator method with acid-base titration. The biodiesel product obtained was analyzed using GCMS. The results of XRD analysis showed that 8% kaolin-methoxide catalyst had the highest crystallinity among the others. The crystallinity obtained was 87.84% with a composition of 15.79% $SiO_2$ and 78.86% $Al_2O_3$. SEM image results also show a more visible crystal shape. The highest basicity of the catalyst obtained was 0.240 mmol. The highest biodiesel yield using 8% kaolin-methoxide catalyst is 99.48%.

**Keywords**

Biodiesel, Catalyst Characterization, Impregnation, Kaolin, Transesterification

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## 1. INTRODUCTION

Along with the increase in population, the need for fuel, especially oil, is also increasing. Meanwhile, petroleum reserves that come from fossils will be increasingly depleted. This is due to this fuel is non-renewable. This fact shows that research based on renewable fuels or better known as biofuels needs to be developed. One of the alternative biofuel energies that is currently being developed is biodiesel. Efforts to develop biodiesel need to be made because it can reduce the burden on communities, especially on small and remote islands, due to high fuel prices and supply uncertainty. The most beneficial thing about biodiesel production is that it can reduce dependence on fossil energy, reduce air pollution and be able to generate environmentally friendly green energy, and of course this energy is available in nature and can be renewed (Khan et al., 2021). Apart from that, biodiesel has advantages over fossil fuels, including that it can be used directly in diesel engines without requiring modification (Sulaiman et al., 2020), low dissolved oxygen content, environmentally friendly, and does not produce CO, sulfur, and NO emissions (Buchori et al., 2016; Singh et al., 2020).

Biodiesel production can be carried out by micro-emulsion using alcohol solvents, cracking, and catalytic-assisted transesterification using short chain alcohols (Zhang et al., 2010). Among these three methods, the best method for producing biodiesel is transesterification. This method will produce fatty acid methyl ester (FAME) (Salaheldeen et al., 2021; Taufiq Yap et al., 2011). The biodiesel production process is carried out using the transesterification method through a reaction between oil derived from plants and alcohol with the help of a catalyst. The catalyst used can be a homogeneous, heterogeneous and enzyme catalyst (Nayab et al., 2022; Mandari and Devarai, 2022). Homogeneous catalysts and enzymes have several disadvantages. The weaknesses of a homogeneous catalyst include the formation of a byproduct in the form of soap, the difficulty of separating biodiesel product with a catalyst, and requiring more water to neutralize it again (Ling et al., 2019; Kibar et al., 2023). Meanwhile, the disadvantages of using enzyme catalysts include high temperature and pressure, expensive enzyme prices, and difficulty in scaling up to a larger scale (Buchori et al., 2016; Pasha et al., 2021). Meanwhile, heterogeneous catalysts have advantages such as: simple product handling (separation and purification), the catalyst is very easy to separate from the system at the end of the process, can be reused, and does not cause soap formation (Ling et al., 2019). For this reason, studies on the use of heterogeneous catalysts in production of biodiesel need to be carried out in order to obtain biodiesel with high purity and easy handling.

Indonesia is a country rich in minerals, one of which is kaolin. This mineral material has not been widely used. So far, kaolin has only been used for building construction. Kaolin is an alumina silicate that contains sources of silica ($SiO_2$), a small amount of iron ($Fe_2O_3$), titanium ($TiO_2$), and alumina ($Al_2O_3$). The large content of octahedral aluminum makes kaolin resistant to acids (Júnior et al., 2013). The chemical and mechanical structure of kaolin is good. In addition, kaolin has a layered structure and good cation exchange capacity. Kaolin contains metals from the alkaline and alkaline earth groups which have the potential to be an active site in making alkaline catalysts (Gao et al., 2015). This fact shows that kaolin has great potential for use in the production process of biodiesel as a catalyst.

Several researchers have used kaolin as a catalyst in production of biodiesel. The use of a zeolite catalyst from geothermal solid waste can produce a biodiesel yield of 98.3% (Buchori et al., 2020). Meanwhile, the use of impregnated hydroxyapatite (HAP) $KI/KIO_3$ catalyst was able to produce a yield of 91.78% (Widayat et al., 2020a). Widayat et al. (2020b) investigated the use of a heterogeneous catalyst of potassium iodide (KI)/$\gamma$-aluminum oxide ($\gamma$-$Al_2O_3$) in production of biodiesel using the esterification method of used cooking oil. The results show the yield of biodiesel of 88.03%. The use of a kaolin catalyst impregnated with NaOH (90 °C for 24 hours) in biodiesel production with palm oil can produce a biodiesel conversion of 95% (Dang et al., 2013). Júnior et al. (2013) synthesized methyl ester from oleic acid with a tungstophosphoric acid catalyst. This catalyst is supported by flint kaolin impregnated using HCl and acetonitrile. This synthesis was operated at 100 °C of temperature and a 2 hours of reaction time resulting in a methyl ester yield of 97.21%. Takase et al. (2023) studied the use of heterogeneous bi-functional Clay-$Na_2CO_3$ catalyst for production of biodiesel. The catalyst is made by impregnation method. The research results showed that the maximum biodiesel yield obtained was 94.7% with transesterification reaction conditions including a 60 °C of reaction temperature of, 2% by weight of catalyst concentration, 12:1 of methanol to oil molar ratio, 1.5 hours reaction time. Meanwhile, research conducted by Abdullahi et al. (2023) showed that the use of KOH-modified metakaolin (KMK) as a heterogeneous catalyst can produce a maximum biodiesel yield was 90.67% under conditions where 5:1 of the molar ratio of methanol/alamanda seed oil, 52.5 °C of reaction temperature, 180 minutes of reaction time and 0.5% wt of catalyst concentration. However, the performance of kaolin as a catalyst is still not optimal in the production process of biodiesel. For this reason, it is necessary to investigate in more depth the most effective method that can be used to optimize kaolin as a catalyst in production of biodiesel. According to Babajide et al. (2012), the $K^+$ ion is a more effective ion when compared to other alkaline earth. This is due to the large molecular size which causes a good pore distribution. Therefore, to improve the performance of kaolin, natural kaolin will be synthesized as a catalyst in biodiesel production by impregnating it with $K^+$ ions. This research aims to examine the effect of KI, $KIO_3$, and kaolin-methoxide impregnation on biodiesel yield. Catalyst characterization was carried out using XRD and SEM. Meanwhile, catalyst stability was tested using recycled catalyst.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

The raw material used in this study is palm oil which is obtained from the local market in Semarang, Indonesia. Kaolin as a source of catalyst is obtained from Gunung Kidul, Yogyakarta, Indonesia. Chemicals obtained from Merck include methanol (99.9%), potassium iodide (KI, 99%), potassium iodate ($KIO_3$, 99.9%), NaOH (pa> 98%, pellets) and Ethylene diamine tetraacetic acid (EDTA). Aquadest obtained from the Diponegoro University Integrated Laboratory.

### 2.2 Catalyst Preparation and Characterization

The catalyst synthesis carried out in this study used the method according to research conducted by Dang et al. (2013). Kaolin obtained from Gunung Kidul, Yogyakarta, Indonesia is cleaned of dirt. Furthermore, kaolin was calcined in a furnace (Ney Vulcan model D-550-240V) at a temperature of 600 °C for 10 hours to remove unwanted components. The calcined kaolin is then impregnated using $KI/KIO_3$. A total of 3.5 grams of kaolin mixed with 7 grams of $KI/KIO_3$ and put into 250 mL of demineralized water. To achieve homogeneity, the mixture was stirred at a stirring speed of 700 rpm while heated at 90 °C for 6 hours. Then, the mixture was deposited for 18 hours. The precipitate was filtered and dried in an oven overnight (Memmert UN 55 B214.0281) at 105 °C. After that, the solid was calcined at 500 °C for 6 hours. The results obtained are $KI/KIO_3$/kaolin catalyst. The catalysts were then characterized by SEM and XRD.

### 2.3 Catalyst Basicity Test

The alkalinity test was carried out using the Hammet indicator method with acid-base titration. The indicator used in this experiment was phenolphthalein. The acid solution used in this experiment was 0.02 mol/L benzoic acid in dry ethanol solvent. The catalyst solid was immersed in 50 mL of methanol, stirred for 1 hour and filtered. The obtained filtrate is dripped with an indicator until it changes color. Furthermore, it is titrated using benzoic acid in a 0.02 mol/L solvent of anhydrous ethanol solution. The titration is stopped when the color of the solution turns clear.

### 2.4 Biodiesel Production

The series of equipment used for experiments in the transesterification process of palm oil using $KI/KIO_3$/kaolin catalyst was shown in Figure 1. Methanol and palm oil with a molar ratio of 12:1 was put into the reactor (three neck flasks). The

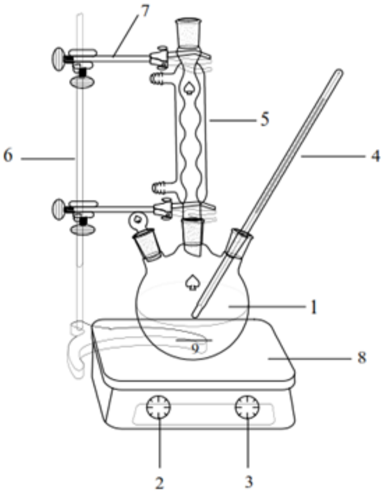

**Figure 1.** The Series of Experimental Equipment for the Transesterification Process: (1) Three-Neck Flask, (2) Thermocontrol, (3) Mixing Regulator, (4) Thermometer, (5) Condenser Reflux, (6) Stative and (7) Clamps

$KI/KIO_3$/kaolin catalyst was placed at the bottom of the three-neck flask. The catalysts were varied at concentrations of 2, 4, 6, 8, and 10%, respectively. For the methoxide catalyst, the kaolin catalyst and methanol are mixed first for 5 minutes, then the kaolin-methoxide catalyst is mixed with palm oil like the treatment for the $KI/KIO_3$ catalyst. The mixture was then heated to a temperature of 70 °C. The temperature was maintained at 70 °C then stirred at 700 rpm. The transesterification process was carried out for 4 hours. The resulting product was then separated from the catalyst by filtering it using a vacuum pump. The remaining methanol contained in the product is separated by distillation at 70 °C. Glycerol and the remaining catalyst which is still present in the biodiesel product were centrifuged at 4000 rpm for 15 minutes. Next, the biodiesel product is placed in the oven for 1 hour to remove any remaining water. The attained biodiesel was analyzed using GCMS.

### 2.5 Measurement of Biodiesel Properties

The biodiesel properties were measured by measuring the parameters of density, viscosity, acid number and saponification number. The density of biodiesel is calculated using Equation (1).

$$\text{Density } \rho = \frac{w_1 - w_2}{V} \tag{1}$$

where $w_1$ = weight of the empty picnometer (gram), $w_2$ = weight of the picnometer containing biodiesel (gram), and V = volume of the picnometer (mL).

The biodiesel viscosity was measured using an Ostwald viscometer. First, 15 ml of distilled water was put into the Ostwald viscometer. Distilled water is sucked until it exceeds the upper limit 's1'. Next, the distilled water is allowed to flow freely. The time required for distilled water to flow from the upper boundary 's1' to the lower boundary 's2' is recorded. This step is repeated to attain the biodiesel viscosity. Biodiesel viscosity is estimated by Equation (2).

$$\eta_x = \frac{\rho_x . t_x}{\rho_a . t_a} \eta_a \tag{2}$$

where $\eta_x$ = biodiesel viscosity; $\eta_a$ = distilled water viscosity; $\rho_x$ = biodiesel density; $\rho_a$ = distilled water density, $t_x$ = time required for biodiesel; $t_a$ = time required by distilled water.

The acid number was measured by titrating the sample with 0.1 N KOH using the PP indicator, where the sample was dissolved first in an organic solvent (ethanol: chloroform 1:1). The KOH volume was recorded when the color of the mixture turned pink. The acid number is calculated using Equation (3).

$$\text{Acid number } = \frac{Mw_{KOH} \times N_{KOH} \times V_{KOH}}{\text{weight of sample (gram)}} \tag{3}$$

where $Mw_{KOH}$ = KOH molecular weight (g/mol); $N_{KOH}$ = KOH normality (mol/mL); $V_{KOH}$ = KOH volume (mL).

The saponification number of biodiesel was estimated by the ASTM D1962 titration method. A fat sample was taken in a chemical glass in the amount of 1 g which was then dissolved in 10 mL of ethanol solvent. Next, 25 mL of 0.5 N KOH ethanol was transferred quantitatively into the fat solvent mixture and was named as the test sample. Blangko samples without fat samples were prepared by the same procedure. Then the two samples were placed in a reflux condenser and heated to the boiling point of water for approximately 30 minutes. After that, the sample was allowed to reach room temperature. Finally, 2-3 drops of phenolphthalein indicator were added to the sample and continued with titration using 0.5 N HCl. The saponification number was calculated using Equation (4).

$$\text{Saponification number } = \frac{M_w \times N \times V_{Blank} \times V_{Test}}{W_s} \tag{4}$$

where $M_W$ = KOH molecular weight (g/mol); N = KOH normality (mol/mL); $V_{Blank}$ = HCl volume for blank sample (mL); $V_{Test}$ = HCl volume for the test sample (mL); $W_S$ = sample weight (g).

The Ca content in biodiesel was measured using an Orion Star T930 ISE Titrator. The electrode, stirrer, and dispenser were rinsed with distilled water. The electrode, stirrer, and dispenser are then placed into the prepared sample in the beaker. The inserted tip of the dispenser is ensured to be below the sample surface. Next, the titration process begins. Enter the sample volume and sample ID when prompted. The reported result is calcium hardness in mg/L $CaCO_3$. If the result is desired in the form of Ca content, then the reported result is multiplied by 40/100.

## 3. RESULTS AND DISCUSSION

### 3.1 Catalyst Characterization

### 3.1.1 XRD Characterization

The catalyst that has been made is then characterized. The results of catalyst characterization using XRD are presented in Figures 2, 3, and 4.

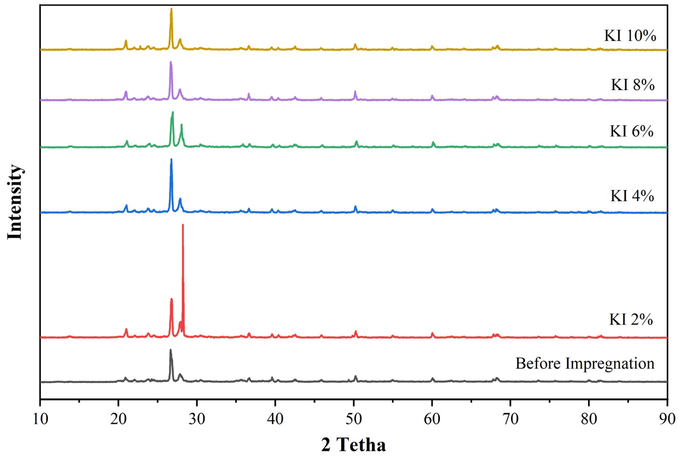

**Figure 2.** The Results of XRD Analysis on KI Impregnated Kaolin Catalyst

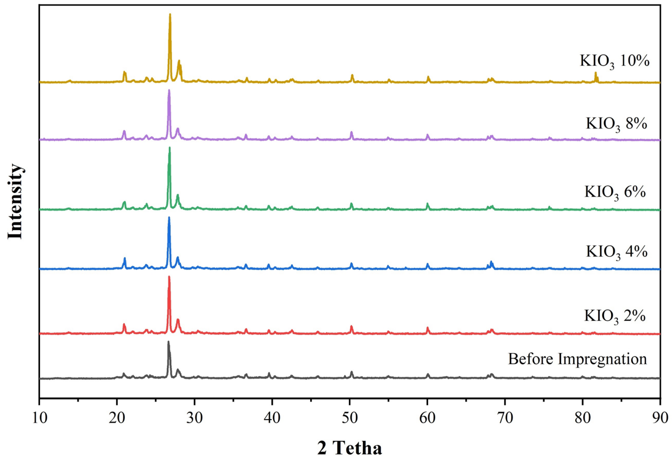

**Figure 3.** The Results of XRD Analysis for $KIO_3$ Impregnated Kaolin catalyst

KI impregnated kaolin catalyst has fluctuating crystallinity. The variable that had the highest crystallinity was kaolin catalyst with the addition of 4% KI, namely 71.26%. Figure 2 does not find any new peaks. This is due to the kaolin before impregnation already containing K, while the impregnation of KI uses a concentration of 2 - 10% by weight of kaolin. The addition of the KI concentration was too small so that it did not have a significant impact.

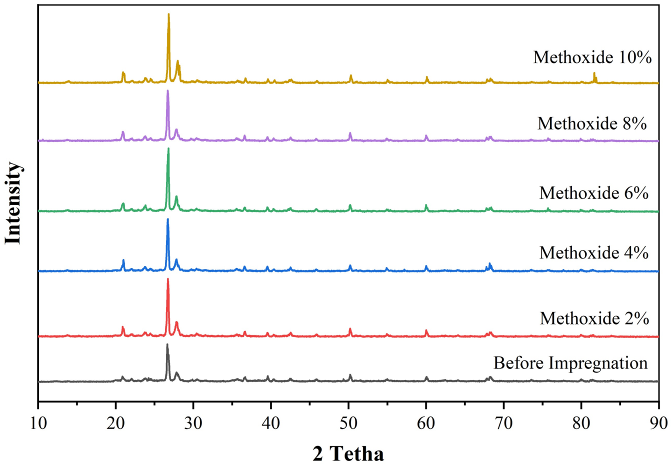

**Figure 4.** The Results of XRD Analysis for Kaolin-Methoxide catalyst

The XRD analysis results of $KIO_3$ impregnated kaolin catalyst are presented in Figure 3. The $KIO_3$ impregnated kaolin catalyst also has a fluctuating crystallinity value. The highest crystallinity was obtained by adding 10% $KIO_3$, which was 81.0%. In Figure 3 no new peaks are found. This is due to kaolin already containing K before impregnation, while $KIO_3$ impregnation using a concentration of 2 – 10% by weight of kaolin is too small so it does not have a significant impact.

The results of the analysis of XRD of the kaolin-methoxide catalyst are presented in Figure 4. The formed kaolin-methoxide catalyst has a fluctuating crystallinity value. The methoxide kaolin catalyst which had the highest crystallinity value was 8% kaolin-methoxide catalyst which was 87.84%.

**Table 1.** The Calculation Results of Crystallite Size (L)

| Variable | L $SiO_2$ |
|---|---|
| KI 2% | 339.7757 |
| KI 4% | 350.4139 |
| KI 6% | 344.8118 |
| KI 8% | 345.6524 |
| KI 10% | 341.4674 |
| $KIO_3$ 2% | 348.8796 |
| $KIO_3$ 4% | 345.6911 |
| $KIO_3$ 6% | 343.6662 |
| $KIO_3$ 8% | 341.5528 |
| $KIO_3$ 10% | 349.7004 |
| Methoxide 2% | 335.8995 |
| Methoxide 4% | 343.8230 |
| Methoxide 6% | 348.3537 |
| Methoxide 8% | 354.3802 |
| Methoxide 10% | 344.4436 |
| Before calcination | 264.8349 |
| After calcination | 235.5842 |

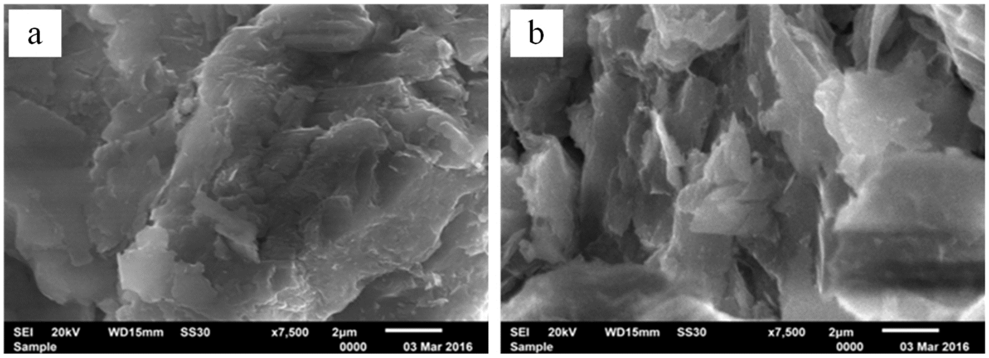

**Figure 5.** SEM Analysis Results of Kaolin: (a) Before Calcination; (b) After Calcination

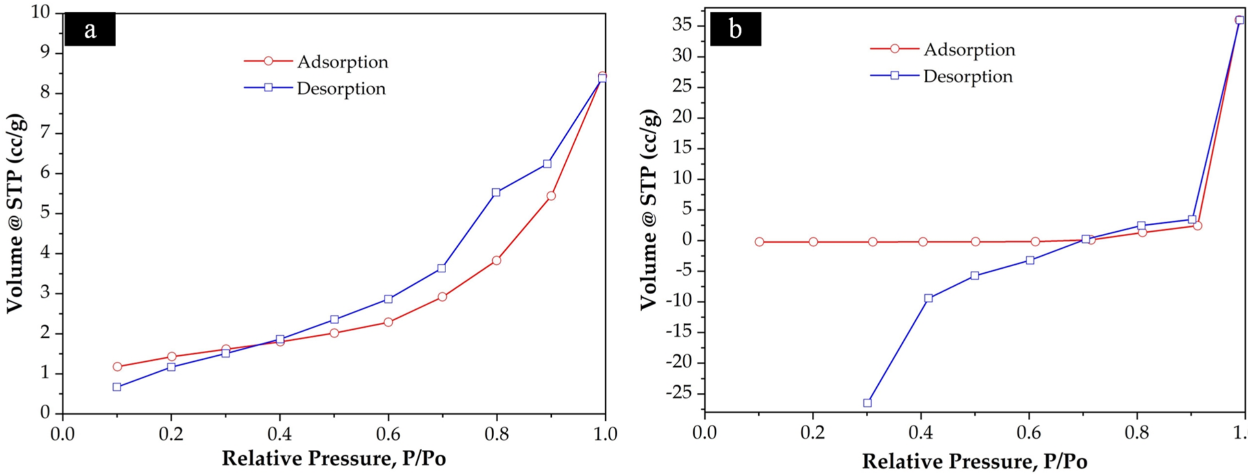

**Figure 6.** Adsorption-Desorption Graph of Kaolin Catalyst : (a) Kaolin Before Calcination; (b) Kaolin After Calcination

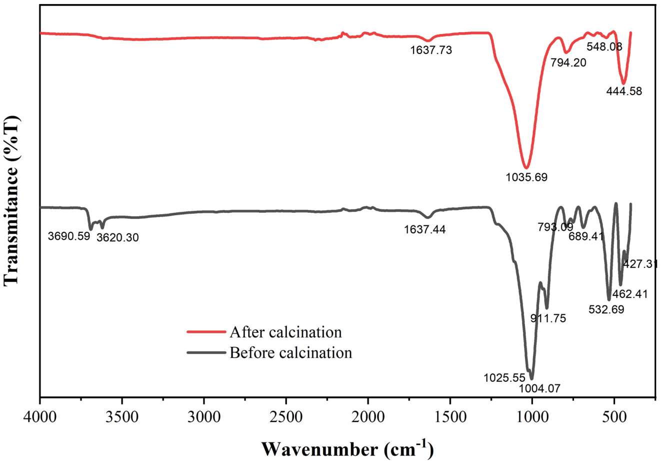

**Figure 7.** IR Spectra of Kaolin

Influential variables can also be seen from the calculation of the crystallite size of $SiO_2$. The results of crystallite size (L) calculations for $SiO_2$ are presented in Table 1. Based on Table 1, the calculation of crystallite size (L) for $SiO_2$ shows that the KI impregnated kaolin catalyst which has the largest value is kaolin with 4% KI impregnation with a value of 350.41. Meanwhile, the $KIO_3$ impregnated kaolin catalyst which had the highest value was 10% $KIO_3$ impregnated kaolin catalyst with a value of 349.70. Table 1 also shows that the kaolin-methoxide catalyst which has the greatest value is 8% kaolin-methoxide catalyst with a value of 354.38. The value of crystallite size (L) is directly proportional to the quality of the crystals formed. The difference in the value of L between one variable and another is not too significant.

### 3.1.2 SEM, BET, and FTIR Characterization

To determine the morphology of kaolin before and after calcining, SEM analysis was carried out. SEM analysis results of kaolin before and after calcination are presented in Figure 5. Calcination is a process of removing organic compounds on the surface of the catalyst which can disturb the active sites through a heating process using a furnace (Yue et al., 2020). Kaolin was calcined at 600 °C for 10 hours. Figure 5 shows that kaolin before calcination does not show pores, while kaolin after calcination has pores and also has a more crystalline surface. This is in line with the results of surface area analysis using BET.

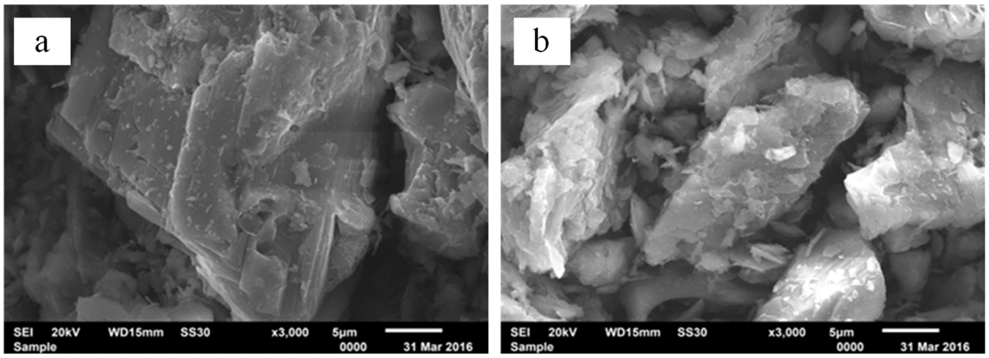

**Figure 8.** SEM Analysis Results: (a) Kaolin Impregnated KIO$_3$10%; (b) Kaolin-Methoxide 8%

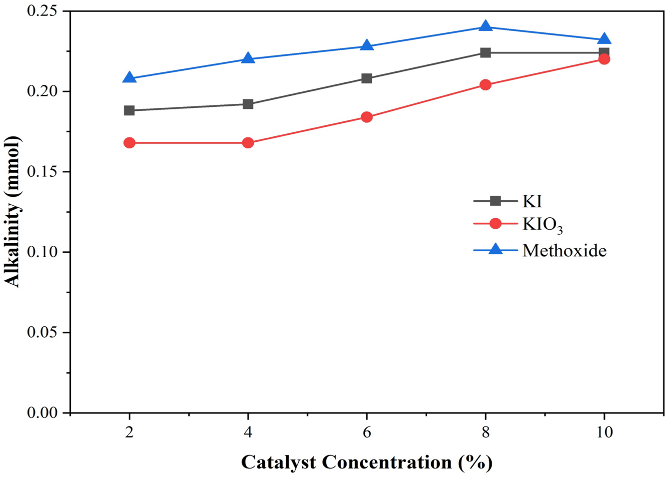

**Figure 9.** Results of the Catalyst Alkalinity Test

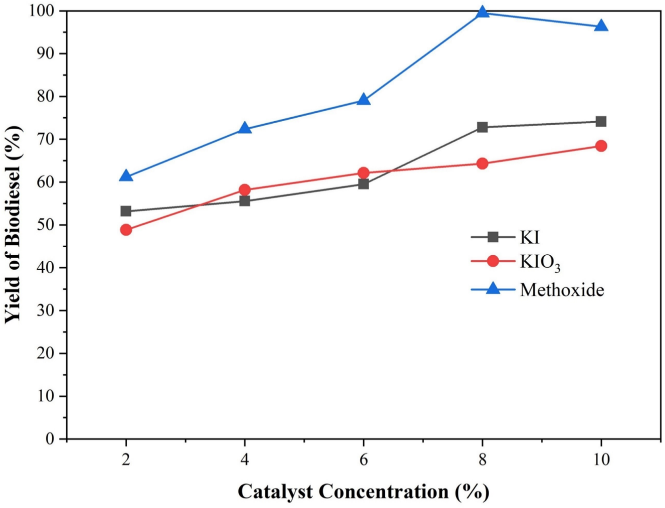

**Figure 10.** Yield of Biodiesel

BET analysis results are presented in Table 2. Adsorption-desorption graph of kaolin catalyst is depicted in Figure 6.

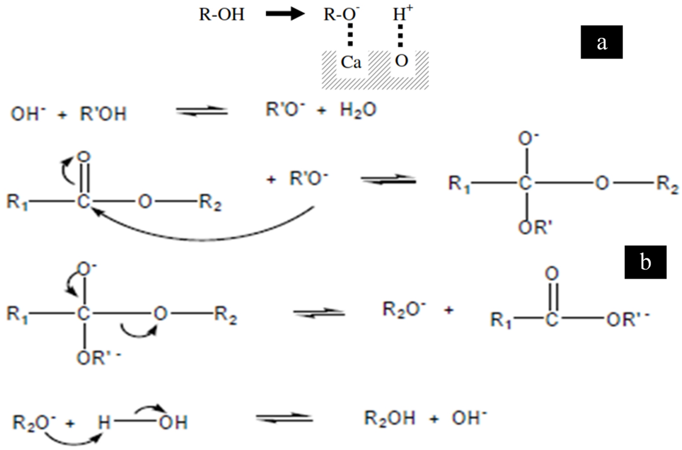

**Figure 11.** The Reaction for the Formation of Methoxide Ions (a); Transesterification Reaction (b) (Kouzu et al., 2008)

Table 2 indicates an increase in pore volume before and after calcination. This is following the results of research conducted by Dang et al. (2013) which stated that the calcination process removes organic compounds that cover the pores on the kaolin surface so that the catalyst surface looks more porous.

In Figure 5a the surface of kaolin before calcination has a fairly flat surface, whereas in Figure 5b, kaolin after calcination has a rougher surface and looks more porous. This is due to after the calcination process, the organic content and impurities in kaolin have been removed so that the surface can look more porous.

Figure 6a is the result of BJH analysis before the kaolin is calcined. It can be seen that the graphs are close to each other, and the two times coincide at one point. Figure 6b is the result of BJH analysis after the kaolin was calcined. It can be seen that the edge of the graph is getting further away. This is because BJH will get better results when analyzing small pore volumes compared to large pore volumes. The smaller the volume, the more the adsorption and desorption graphs coincide.

The FTIR spectrum of kaolin and calcined kaolin are depicted in Figure 7. Figure 7 indicates that the characteristic peaks of kaolin are shown at 3690.59 cm$^{-1}$ and 3620.30 cm$^{-1}$,

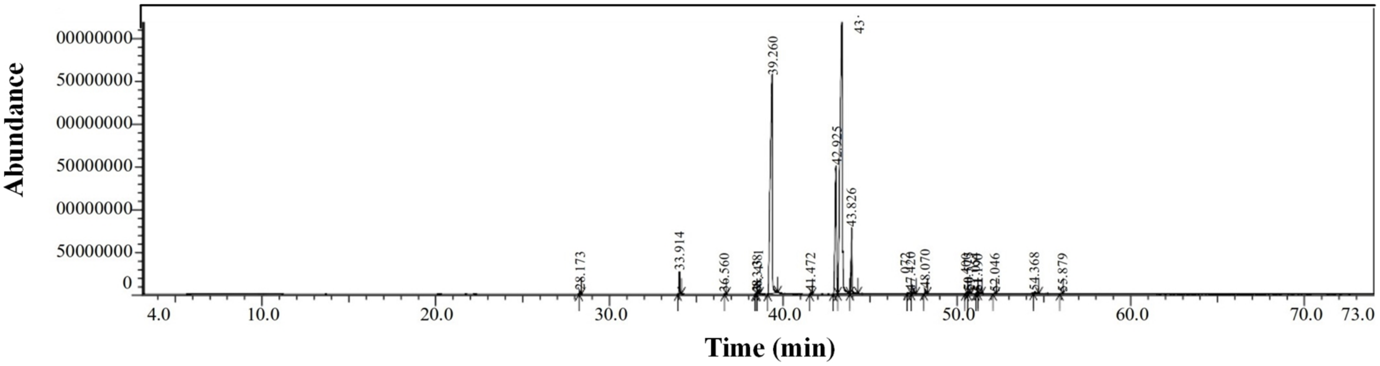

**Figure 12.** Results of Analysis of Biodiesel with 8% Kaolin-Methoxide Catalyst

**Table 2.** BET Analysis Results of Kaolin

| Material | Pore Volume (cc/g) | Surface Area ($m^2/g$) | Pore Diameter (A) |
|---|---|---|---|
| Kaolin before calcination | 0.013 | 5.514 | 43.913 |
| Kaolin after calcination | 0.084 | 26.567 | 18.080 |

corresponding to OH-stretching vibrations. The $H_2O$ stretch is found at 1637.44 $cm^{-1}$. The Si−O bonds are assigned to the 1025.55 $cm^{-1}$ and 1004.07 $cm^{-1}$ bands. The band at 911.75 $cm^{-1}$ is attributed to $Al^{IV}$−OH vibrations. Meanwhile, the bands at 793.09 $cm^{-1}$ and 689.47 $cm^{-1}$ are symmetrical Si−O stretches. The absorption at 532.69 $cm^{-1}$ is determined as Si−O−$Al^{VI}$, where Al is in octahedral coordination (Liew et al., 2012).

After the kaolin is calcined, the $OH^-$ vibration peak disappears, indicating that the calcination of the kaolin into calcined kaolin is complete. The $H_2O$ stretch at 1637.73 $cm^{-1}$ is still there. The Si−O kaolin band was still detected at 1035.69 $cm^{-1}$ but was higher than before calcination. The $Al^{IV}$−OH absorption band disappears due to the distortion of tetrahedral and octahedral kaolinite sheets (Liew et al., 2012). Si−O symmetric stretching is found in the 794.20 $cm^{-1}$ band. Meanwhile, the 532.69 $cm^{-1}$ band was switched to a higher frequency after the calcination process.

Figures 8a and 8b are a comparison of the results of kaolin characterization using SEM. Figure 8a is an SEM image of kaolin impregnated with 10% $KIO_3$ with the highest crystallinity. Figure 8b is an SEM image for kaolin methoxide which has the highest crystallinity in the kaolin-methoxide variable. From a comparison of the 2 images, it is obtained that Figure 8b has a rougher surface image and looks more porous than Figure 8a.

### 3.1.3 Catalyst Alkalinity Test

The results of the catalyst alkalinity test are presented in Figure 9. From the results of the catalyst alkalinity test (Figure 9) it was found that the catalyst that had the highest alkalinity was 8% kaolin-methoxide catalyst, namely 0.240 mmol. Meanwhile, 10% kaolin-methoxide catalyst has lower alkalinity compared to 8% kaolin-methoxide catalyst, although the values obtained are not much different. This is due to the almost the same number of K ions present on the surface of the 8% kaolin-methoxide and 10% kaolin-methoxide catalysts so that with the same time and treatment, the methoxide ions formed also have almost the same amount (Xie et al., 2006). Impregnation of kaolin using KI and $KIO_3$ gives the same result, that is, the more KI and $KIO_3$ used, the catalyst's alkalinity value increases because the number of impregnated K ions also increases, although with a small difference.

### 3.2 Biodiesel Product and Characterization

The main component of biodiesel is methyl ester. The more methyl esters formed, the better the quality of the biodiesel product. Analysis of methyl ester content was carried out using GCMS (Gas Chromatography Mass Spectro). GCMS analysis used Shimadzu type TQ-8060 with 5ms TRX column type. The concentration of methyl ester and yield of biodiesel formed can be calculated using the Equations (5) and (6).

$$\text{ME Concentration (\%)} = \frac{\text{Area of Methyl Ester}}{\text{Area of Standard Methyl Ester} \times \text{ME}} \text{Standard Concentration (\%)} \qquad (5)$$

$$\text{Yield of Biodiesel (\%)} = \frac{\text{Biodiesel Product Mass (g)}}{\text{Feed Mass (g)} \times \text{ME Concentration(\%)}} \qquad (6)$$

The area of the methyl ester is calculated based on the GCMS data obtained, so that the biodiesel yield data can be obtained (Figure 10). Figure 10 shows that the highest yield of biodiesel was achieved using 8% kaolin-methoxide catalyst. In biodiesel production using KI and $KIO_3$ impregnated kaolin catalysts, the yield of biodiesel increased with the addition of KI and $KIO_3$. This is due to the more KI and $KIO_3$ used for impregnation, the more it will stick to the surface of the kaolin.

**Table 3.** Results of GCMS Analysis of Biodiesel Components with 8% Kaolin-Methoxide Catalyst

| Peak | R. Time (min) | Area (%) | Component |
|---|---|---|---|
| 1 | 28.173 | 0.17 | Dodecanoic acid, methyl ester (CAS) |
| 2 | 33.914 | 1.18 | Tetradecanoic acid, methyl ester (CAS) |
| 3 | 36.560 | 0.03 | Pentadecanoic acid, methyl ester (CAS) |
| 4 | 38.338 | 0.03 | 9-Hexadecenoic acid, methyl ester, (2)-(CAS) |
| 5 | 38.431 | 0.21 | 9-Hexadecenoic acid, methyl ester, (2)-(CAS) |
| 6 | 39.260 | 32.60 | Hexadecanoic acid, methyl ester (CAS) |
| 7 | 41.472 | 0.08 | Hexadecanoic acid, methyl ester (CAS) |
| 8 | 42.925 | 13.19 | 9,12-Octadecadienoic acid (Z,Z)-, methyl ester (CAS) |
| 9 | 43.284 | 46.77 | 9-Octadecenoic acid (Z)-, methyl ester (CAS) |
| 10 | 43.826 | 4.50 | Octadecanoic acid, methyl ester (CAS) |
| 11 | 47.072 | 0.15 | Hexadecanoic acid, 2-hydroxy-1,3-propanedyil ester (CAS) |
| 12 | 47.420 | 0.12 | 11-Eicocenoic acid, methyl ester (CAS) |
| 13 | 48.070 | 0.25 | Eicosanoic acid, methyl ester (CAS) |
| 14 | 50.400 | 0.05 | Ethyl linoleate |
| 15 | 50.575 | 0.14 | 9-Octadecenal, (Z)-(CAS) |
| 16 | 51.054 | 0.16 | Hexadecanoic acid, 2-hydroxy-1-(hydroxy methyl)ethyl ester (CAS) |
| 17 | 51.190 | 0.10 | Butyl 10-undecenoate |
| 18 | 52.046 | 0.04 | Docosanoic acid, methyl ester (CAS) |
| 19 | 54.368 | 0.17 | 9-Octadecenoic acid (Z)-, 9-octadecenyl ester (CAS) |
| 20 | 55.879 | 0.05 | Tetracosanoic acid, methyl ester (CAS) |
|  |  | 100 |  |

The results of this research follow the results of the basicity characterization test which shows that the more KI and $KIO_3$ used for impregnation, the more basic sites there are on the catalyst (Xie et al., 2006).

The highest biodiesel yield achieved using 8% kaolin-metho xide catalyst was 99.48%. In the manufacture of kaolin-metho xide, the added methanol completely reacts with the alkali ions present in the kaolin to form kaolin-methoxide. According to Júnior et al. (2013), the true catalyst for biodiesel production is a methoxide catalyst because the methoxide ions formed will attack the hydroxyl groups present in triglycerides. The reaction mechanism can be shown from Figure 11.

From the results of the catalyst alkalinity test in Figure 9, 8% kaolin-methoxide catalyst has the highest alkalinity value. This causes the 8% kaolin-methoxide catalyst to have large amounts of alkali or alkaline earth metals and promotes the formation of methoxide ions (Xie et al., 2006). In Table 1, 8% kaolin-methoxide catalyst has the highest crystallite size. This is evidence that the kaolin catalyst crystals form well compared to other catalyst variables.

In the production of biodiesel using a 10% kaolin-methoxide catalyst, the biodiesel yield decreased but not significantly, namely 96.27%. This is due to under the same operating conditions, the methoxide ions formed are the same as the 8% kaolin-methoxide catalyst so that when testing the use of the catalyst in the transesterification reaction, the yield of biodiesel obtained is almost the same as the 8% kaolin-methoxide catalyst. The results of analysis of biodiesel products using GCMS with 8% kaolin-methoxide catalyst are presented in Figure 12 and Table 3.

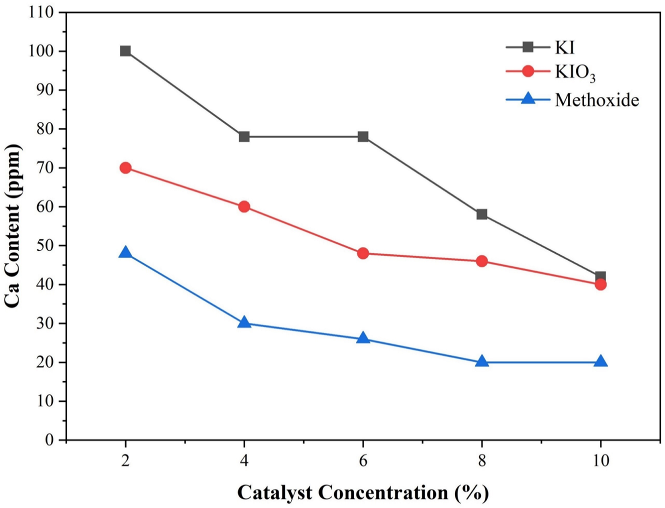

**Figure 13.** Results of Analysis of Ca Content in Biodiesel

Figure 12 and Table 3 show that biodiesel produced with 8% kaolin-methoxide catalyst produces large amounts of methyl esters. This is due to almost all triglycerides are converted into methyl esters in the transesterification reaction using 8% kaolin-methoxide catalyst.

**Table 4.** Results of Measurement of the Physical Properties of Biodiesel Products

| Variable | Density (kg/m$^3$) | Viscosity (cst) | Acid Number (mg KOH/g) | Saponification Number |
|---|---|---|---|---|
| Kaolin-KI 2% | 920 | 5.34 | 0.3 | 187 |
| Kaolin-KI 4% | 890 | 4.34 | 0.3 | 188 |
| Kaolin-KI 6% | 850 | 4.22 | 0.2 | 188 |
| Kaolin-KI 8% | 875 | 4.22 | 0.2 | 188 |
| Kaolin-KI 10% | 888 | 3.96 | 0.2 | 190 |
| Kaolin-$KIO_3$ 2% | 890 | 5.34 | 0.3 | 184 |
| Kaolin-$KIO_3$ 4% | 850 | 4.34 | 0.3 | 185 |
| Kaolin-$KIO_3$ 6% | 880 | 4.22 | 0.3 | 185 |
| Kaolin-$KIO_3$ 8% | 880 | 3.52 | 0.2 | 185 |
| Kaolin-$KIO_3$ 10% | 880 | 3.96 | 0.2 | 186 |
| Kaolin-methoxide 2% | 850 | 4.34 | 0.3 | 186 |
| Kaolin-methoxide 4% | 877 | 4.03 | 0.2 | 187 |
| Kaolin-methoxide 6% | 885 | 3.81 | 0.2 | 188 |
| Kaolin-methoxide 8% | 880 | 3.61 | 0.2 | 190 |
| Kaolin-methoxide 10% | 885 | 3.81 | 0.2 | 190 |

**Table 5.** Comparison of the Performance of Kaolin-Methoxide Catalyst with Other Catalysts in the Production of Biodiesel

| Feedstock | Catalyst | Catalyst Amount | Reaction Time (h) | Reaction Temperature (°C) | Yield (%) | References |
|---|---|---|---|---|---|---|
| Palm oil | Kaolin- methoxide | 8% | 4 | 70 | 99.48 | This study |
| Palm oil | Metakaolin | 10% | 2 | 63 | 95.4 | (Dang et al., 2013) |
| Oleic acid | Metakaolin flint | 20% | 2 | 100 | 97.21 | (Júnior et al., 2013) |
| Used cooking oil | Zeolite | 5% | 1 | 300 | 98.299 | (Buchori et al., 2020) |
| Waste cooking oil | KI/-$Al_2O_3$ | 2% | 3 | 65 | 88.03 | (Widayat et al., 2020a) |
| Waste cooking oil | HAP/KI/$KIO_3$ | 5% | 6 | 60 | 91.78 | (Widayat et al., 2020b) |
| Allamanda seed oil | KOH-modified metakaolin (KMK) | 0.5% | 3 | 52.5 | 90.67 | (Abdullahi et al., 2023) |
| Parkia biglobosa oil | Clay-$Na_2CO_3$ catalyst | 2% | 1.5 | 60 | 94.7 | (Takase et al., 2023) |
| Neem seed derived oil (NSDO) | Nano hydrophobic sulfated mordenite | 6% | 1 | Ambient | 85 | (Karimi and Saidi, 2024) |

### 3.3 Properties of Biodiesel Product

The properties of biodiesel were measured by measuring the parameters of density, viscosity, acid number and saponification number. The results of the analysis of the properties of biodiesel are presented in Table 4.

The standards used in measuring the physical properties of biodiesel are SNI 7182-2015 and EN 14214-2012. According to SNI, the density of biodiesel is 850-890 kg/m$^3$, the viscosity is 2.3-6 mm$^2$/s, and the maximum acid number is 0.5 mg KOH/g. Meanwhile, according to EN 14214-2012, the density of biodiesel is 860-900 kg/m$^3$, the viscosity is 3.5-5 mm$^2$/s, and the maximum acid number is 0.5 mg KOH/g.

The results of biodiesel density measurements show that almost all biodiesel densities meet SNI and EN standards. Only one variable exceeds the standard, namely biodiesel using 2% KI impregnated kaolin catalyst. This is due to the large amount of cooking oil that has not been converted into biodiesel. The viscosity of biodiesel products measured is in accordance with SNI. However, some do not meet EN standards, namely, biodiesel produced using a kaolin catalyst impregnated with KI 2% and $KIO_3$ 2% where the results exceed the standard. This is because cooking oil has not been converted into biodiesel. This result is in line with the density measurement where when there is still a lot of cooking oil that has not been converted into biodiesel, the density exceeds the SNI standard. The acid number is the amount of KOH used to neutralize the amount of acid present in the oil. In biodiesel, the better the quality, the smaller the acid number. The results of measuring the acid number of biodiesel show that all variables have acid numbers that comply with SNI and EN standards. Biodiesel production using a kaolin-methoxide catalyst tends to have a low acid number. The saponification number is the amount of KOH used to saponify 1 gram of oil or fat. Biodiesel is considered to be better if the saponification rate is higher. On the results of biodiesel measurements, it was found that the results of measurements of the saponification rate showed almost the same number. The difference between one biodiesel and another is not too big. The saponification number obtained is within the

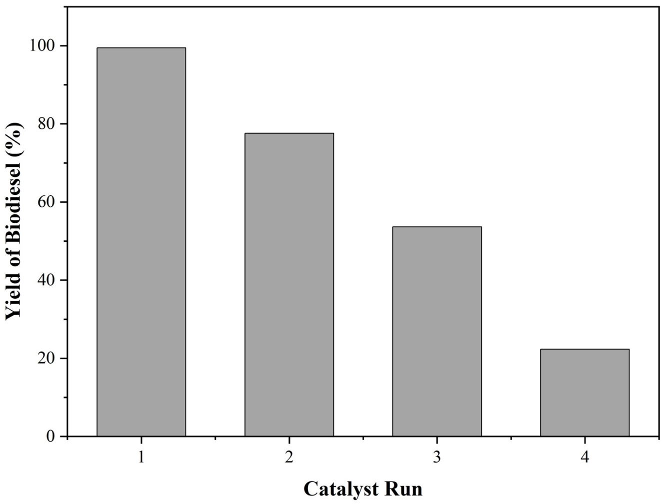

**Figure 14.** Yield Biodiesel on Fresh and Reused Catalysts

range of the saponification number according to O'Brien et al. (2005) that is equal to 189 – 197 mg KOH/g.

### 3.4 Analysis of Ca Content in Biodiesel Products

The results of the analysis of Ca content in biodiesel products are presented in Figure 13. The content of Ca in biodiesel indicates the presence of basic sites on biodiesel. The Ca content in biodiesel needs to be checked. This calcium can be reacted with carbon dioxide produced from the combustion of biodiesel. As a result, calcium carbonate can be deposited and fouling in the machine.

Biodiesel produced using KI and $KIO_3$ impregnated kaolin catalysts tends to have a fairly high Ca content. While the biodiesel produced with the kaolin-MeOH catalyst has a lower Ca content. This is due to in the kaolin-MeOH catalyst, kaolin is converted to methoxide so that the reaction becomes more efficient. The low Ca content indicates that Ca as an alkaline site reacts well so that the remaining Ca content in biodiesel is small.

### 3.5 Reusability Catalyst

The advantage of using heterogeneous catalysts in the industry is that it is easier separation and can be reused. Separation of heterogeneous catalysts can easily be done through filtration using a vacuum to obtain more optimal results. The catalyst regeneration is done by rinsing the catalyst using hexane and continuing drying in the oven at 100 °C for 12 hours.

In the catalyst reuse test, the catalyst used was 8% kaolin-methoxide catalyst because this catalyst had the highest yield in the biodiesel production trial. The results of catalyst reusability are presented in Figure 14. In Figure 14, the yield of biodiesel has decreased in proportion to the reuse of the catalyst. This is due to the catalyst is deactivated. In addition, the catalyst was poisoned by glycerol and the presence of soap products in the reaction mixture (Rahim et al., 2020). The reduced number of $K^+$ ions is also one of the reasons for the decreased yield of biodiesel obtained.

The results of this study compared with other researchers are presented in Table 5. Table 5 contains the results of previous research investigating the use of various catalysts to produce biodiesel. The catalyst used in this study provided higher biodiesel yields compared to most studies. A high yield (98.29 9%) was obtained by Buchori et al. (2020) used a zeolite catalyst but required a high reaction temperature (300 °C). Likewise, the metakaolin flint catalyst used by Júnior et al. (2013) also gave quite high biodiesel yields (97.21) but required a large amount of catalyst and a higher reaction temperature. Karimi and Saidi (2024) succeeded in using ambient temperature in their research, but the resulting yield was quite low, namely only 85%. These results prove that the kaolin-methoxide catalyst used in the research is very effective for producing biodiesel with high yields.

## 4. CONCLUSIONS

The results in this study showed that the results of the XRD analysis showed no addition of new peaks because before impregnation the kaolin already contained K ions. The reaction of methanol and $K^+$ ions could not be detected using XRD. Calculation of the crystallite size (L) for $SiO_2$ showed that the kaolin-methoxide catalyst with the highest value was 80% kaolin-methoxide catalyst with a value of 354.38. The value of L is directly proportional to the quality of the crystals formed. The morphological SEM images of kaolin before and after calcination show that before calcination, kaolin does not show any pores, while after calcination it appears to have pores and also has a more crystalline surface. The results of the catalyst alkalinity test showed that the catalyst with the highest alkalinity was 8% kaolin-methoxide catalyst, which was 0.24 mmol. The results of testing the physical properties of biodiesel, which includes density, viscosity, acid number and saponification rate show compliance with SNI and EN standards. Only kaolin catalyst impregnated with 2% KI and 2% $KIO_3$ did not meet SNI and EN standards because the transesterification reaction had not occurred completely. The highest biodiesel yield in biodiesel production was achieved using 8% kaolin-methoxide catalyst, namely 99.48

## 5. ACKNOWLEDGMENT

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