Synthesis of Biodiesel from Low-Quality Crude Palm Oil with Heterogeneous Catalyst CaO-ZnO

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Abstract: Synthetic optimization of methyl ester has been extracted from low-quality crude palm oil using heterogeneous catalyst. Quantitatively, the crude palm oil with low-quality is in abundance. To prepare the raw material to be used for biodiesel, it requires to be refined beforehand. By using heterogeneous catalysts, the synthetic biodiesel would become more affordable and environmentally friendly. This study aimed to synthesize methyl esters from low-quality crude palm oil using CaO-ZnO catalyst and determine its potential as biodiesel. This research was carried out through several stages, namely refining low-quality crude palm oil, determining the levels of low-quality refined crude palm oil free fatty acids, esterification, synthesis of methyl esters from low-quality crude palm oil with CaO-ZnO catalyst through transesterification, identification of the components composition of the mixture of synthesized methyl ester by GC-MS, and the characterization of the synthesized methyl esters. The results showed that methyl esters could be synthesized from low-quality crude palm oil through a transesterification reaction using CaO-ZnO catalyst. The highest yield was obtained from the use of catalyst 4% w/w of oil with a yield of 84.74%. The components of the constituent compounds of the mixture of synthesized methyl ester were methyl myristate (2.72%), methyl palmitate (54.87%), methyl linoleic (5.78), methyl oleate (26.83%), and methyl stearate (2.55%). The results of the characterization of the synthesized methyl ester showed a density 0.876 g/mL, a viscosity 3.60 cSt, a refractive index 1.448, and an acid number of 0.39 mg KOH/g of methyl ester, resulting in the potential methyl ester as biodiesel.

Keywords: methyl ester, crude palm oil, transesterification, CaO-ZnO catalyst, biodiesel

1. Introduction
Petroleum fuel is one of the main energy sources used by the community. If the level of community welfare increases, the need for petroleum as a fuel will be higher as well. Therefore, it is necessary to develop renewable alternative energy, such as biodiesel. Biodiesel is an alternative fuel produced from vegetable oils or animal fats. Vegetable oils that can be used as biodiesel include crude palm oil, tobacco seeds, jatropha curcas, soybeans, and sunflower seed oil. Biodiesel derived from vegetable oils is non-toxic, biodegradable, and environmentally friendly which can be produced through transesterification reactions [1].

Indonesia is one of the largest crude palm oil producing countries in the world. Crude palm oil is a commodity that has the potential as biodiesel due to the fact that its presence is pretty much abundant.
However, not all crude palm oils have good-quality. The low-quality crude palm oil has a high profit and adds selling value when it is used as a more useful material [2]. Therefore, there are opportunities for the low-quality crude palm oil to be processed into more useful ingredients. The low-quality crude palm oil that has high levels of free fatty acids can be reduced through the purification process. This purification process aims to reduce the level of oil viscosity, absorb color, the levels of free fatty acids so as to facilitate the synthesis of methyl esters through the transesterification method. The purification process can be carried out through bleaching stages using adsorbents including activated carbon, natural zeolite, and silica.

Transesterification is a reaction process of the formation of methyl esters from triglycerides with the help of alkyl alcohol and by-products obtained in the form of glycerol. Methanol is more often used because it has a higher reaction rate compared to other types of alcohol and the price is relatively cheap [3]. Transesterification can take place if the level of oil free fatty acids is less than 2%. However, if the free fatty acid level is more than 2%, the esterification process is carried out first [4]. The esterification stage requires an acid catalyst such as H$_2$SO$_4$ while the transesterification catalyst commonly used is a homogeneous catalyst such as NaOH and KOH. Homogeneous catalysts have many weaknesses that are considered less effective. To overcome these problems, heterogeneous catalysts are used. The types of heterogeneous catalysts that can be used in transesterification are metal oxides such as CaO, ZnO, MgO, K$_2$O [5].

CaO catalysts are heterogeneous catalysts often used because they have high activeness, are low in price, and have high base strength but have a slightly soluble nature in methanol [2]. ZnO can function as a catalyst and can also be a good catalyst support in the transesterification reaction so as to increase the yield of methyl esters [1]. CaO is slightly soluble in methanol, this can affect the final result which will slightly inhibit the separation process so that the combination of CaO with ZnO can protect the active phase of CaO in reaction media because of the strong interaction between the active side and catalyst support [6]. The use of CaO-ZnO catalyst can improve the basic properties of the catalyst so that it is expected to obtain optimum methyl ester yield. The use of CaO-ZnO catalyst is thought to have the potential to be applied to crude palm oil as a biodiesel material.

This study aimed to synthesize methyl esters from low-quality crude palm oil using CaO-ZnO catalyst. In addition, this study also aimed to determine the components of methyl esters synthesized from low-quality crude palm oil using CaO-ZnO catalyst and to understand the characteristics of methyl esters produced from low-quality crude palm oil and its potential as biodiesel.

2. Methods

2.1. Characterization of CaO-ZnO Catalyst

Initially, the solid form of CaO was dissolved in demineralized water. Then, ZnO solids were added to the solution with a ratio of CaO:ZnO of 1:2 [5]. The mixture was stirred using a magnetic stirrer until homogeneous for 3 hours. The precipitate formed was then filtered and placed in an oven at 110 °C for 24 hours. Then, the CaO-ZnO in powder form was calcined at 300 °C for 2 hours [7]. The obtained CaO-ZnO catalyst was characterized using XRD.

2.2. Refinement of Low-Quality Crude Palm Oil

This crude palm oil needs to be refined to reduce the levels of free fatty acids. The refinement process was carried out by adding 2% w/w of HCl activated zeolite to 100 g of the crude palm oil. The refinement process was assisted with a hotplate magnetic stirrer while heated at 170 °C for 1 hour. Furthermore, the crude palm oil was centrifuged at 3000 rpm for 20 minutes.

2.3. Determination of Low-Quality Free Fatty Acid Levels of the Refined Crude Palm Oil

Determination of free fatty acids was done by titration method. As much as 1.00 g of refined crude palm oil was put into Erlenmeyer. Then, 5 mL of 95% ethanol was added and the phenolphthalein indicator was 3 drops. The solution was titrated using 0.1 M KOH solution until it was pink color. The KOH
solution was recorded in volume to determine the levels of the crude palm oil free fatty acids [8]. The test was repeated twice.

2.4. Esterification
A total of 50.0 g of refined crude palm oil was put in a three-neck flask. Methanol was then added with a mole ratio of oil: methanol, which was 1:12. Subsequently, it was heated while stirring by using a hotplate magnetic stirrer. After the temperature reached 30 °C, the catalyst was added in the form of sulfuric acid at 1% w/w. Then, the temperature was set to be constant at 60-65 °C. Stirring lasted for 1 hour. Then, the esterification results were inserted into a separated funnel and allowed to stand for 24 hours until a layer was formed. The bottom layer obtained was then washed with warm water and heated at 80-100 °C. The esterification results that had been washed were then added with anhydrous magnesium sulfate to remove the remaining water [7].

2.5. Synthesis of Methyl Ester from Low-Quality Crude Palm Oil with CaO-ZnO Catalyst through Transesterification
The synthesis of methyl ester from the crude palm oil was carried out through a process which was transesterification with the help of heterogeneous CaO-ZnO catalyst. A total of 20.0 g of the crude palm oil was poured into a three-neck flask. Methanol was added with a mole ratio of oil: methanol, being 1:15 and catalyst with various concentrations (3%; 4%; 5%) w/w. The mixture was refluxed for 3 hours at 65 °C with stirring speed of 300 rpm. The mixture was centrifuged at a speed of 3000 rpm for 20 minutes. Then, the mixture was placed in a separated funnel and allowed to separate methyl esters and glycerol. The results of the separation were formed in two layers, namely, the top layer was yellow methyl ester, and the lower layer was brown glycerol. The methyl esters formed were then washed using warm water to dissolve the remaining catalyst, methanol, and glycerol. After washing, methyl esters were heated and anhydrous was added in the form of MgSO₄ which functioned to absorb water.

2.6. Identification of the Synthesized Methyl Ester Components with GC-MS
Identification using GC-MS was carried out to determine the components of compounds formed from transesterification in the form of methyl esters. GC-MS identification was carried out at a column flow rate of 0.45 ml/min, a temperature of 40-280 °C, at a pressure of 10.9 kPa. The results were obtained in the form of spectrum peaks from the results of injection of crude palm oil. In addition, analysis using GC-MS can provide information on the molecular structure and molecular weight of each of the constituent components of methyl esters [9,10].

2.7. Characterization of Methyl Esters
The synthesized methyl ester with a transesterification reaction alkaline catalyst from palm oil was characterized including density, viscosity, and acid number. The physical properties of the synthesized methyl esters were matched with the physical properties of biodiesel in SNI biodiesel to determine their potential as biodiesels.

3. Results and Discussion

3.1. Preparation and Characterization of CaO-ZnO Catalyst
The catalyst used in the study was a heterogeneous base catalyst in the form of CaO and ZnO. The composition of the catalyst combination was used with a ratio of CaO:ZnO of 1:2. The combination of CaO and ZnO catalyst can increase catalyst activity and protect the active side of CaO by strong interaction with ZnO so that it does not dissolve in the reaction medium [11]. The catalyst was calcined at 300 °C for 2 hours. This calcination process aimed to open the pores of the catalyst so that it accelerated the transesterification reaction. CaO-ZnO catalyst from white powder formations, which were then characterized using XRD instrument. The results of characterization were compared with CaO standard diffractogram according to JCPDS Card No. 37-1497 and ZnO standard diffractogram.
according to JCPDS Card No. 36-145. The XRD diffractogram of CaO-ZnO catalyst can be seen in Figure 1.

Figure 1 shows that the XRD pattern of CaO-ZnO was indicated by the peaks that corresponded to JCPDS Card No. 37-1497 (CaO) and JCPDS Card No. 36-1451 (ZnO). The peaks at an angle of 2\( \theta \) which corresponded to JCPDS Card No. 37-1497 (CaO) were 18.00°, 28.71°, 31.78°, 34.04°, 54.36°, 66.4°, and the peaks at 2\( \theta \) which corresponded to JCPDS Card No. 36-1451 (ZnO) were 34.44°, 36.26°, 47.56°, 56.61°, 62.87°, 67.95°, 69.12°, and 77.05°. The results of the analysis using x-ray diffraction found a new peak at 50.79° with a low-intensity which was suspected to be an impurity formed during the synthesis of CaO-ZnO catalyst.

![XRD diffractogram of CaO-ZnO catalyst](image)

**Figure 1.** The XRD diffractogram of CaO-ZnO catalyst

3.2. Refined Low-Quality Crude Palm Oil
The low-quality crude palm oil was refined by adding 2% active zeolite in 100.00 g of oil and heated at 170 °C for 1 hour. The refining process aimed to reduce impurities contained in the oil. These impurities were such as free fatty acids, color, and smell. The physical appearance of the low-quality crude palm oil before and after refining is shown in Figure 2. It shows that the physical appearance of quality crude palm oil in low quality crude palm oil before refining has a red color, as compared to after refinement, indicated by yellow color. The smell of low quality crude palm oil before and after was changed.

![Low-quality crude palm oil before and after refinement](image)

**Figure 2.** CPO before refinement (left side) and CPO after refinement (right side)
3.3. Esterification

The low-quality crude palm oil used in the transesterification process must have free fatty acid levels < 2%, while the low-quality crude palm oil produced by the refined crude palm oil used in this study still had high free fatty acid levels of 7.96% [11]. The results of esterification showed that the levels of free fatty acids from transesterification <2% were 0.93% so that they could be used in the transesterification process. The smaller level of free fatty acids, the more likely it will be to form soap.

3.4. Synthesis of Methyl Ester from Low-Quality Crude Palm Oil with CaO-ZnO Catalyst through Transesterification

The synthesis of methyl ester from the low-quality crude palm oil was carried out through transesterification using alcohol, in the form of methanol and alkaline catalyst, such as CaO-ZnO. This transesterification process was carried out in duplicate using conventional methods namely using reflux to produce new esters and alcohol.

A total of 20.00 g of esterified oil was heated in a three-neck flask to a temperature of 60-65 °C. Then, a mixture of methanol and CaO-ZnO catalyst was added and refluxed at 65 °C for 3 hours. The mole ratio of oil:methanol used was 1:15 and the CaO-ZnO catalyst used was 3%, 4%, and 5% w/w.

The mechanism of the low-quality crude palm oil transesterification reaction is as follows:

Stage 1. The Formation of Methoxide Ions by Catalysts and Methanol

\[ \text{H}_3\text{C} \text{OH} + \text{B} \overset{\text{O}}{\longrightarrow} \text{OCH}_3 \text{H} \]

Stage 2. The Formation of Digliseride and Methyl Ester

\[ \text{R}_1\text{COO} \overset{-}\text{CH}_2 + \text{CH}_2\overset{-}\text{O} \text{CR}_3 \overset{\text{O}}{\longrightarrow} \text{R}_1\text{COO} \overset{\text{CH}}{-} \text{CH}_2\overset{-}\text{O} \overset{\text{O}}{\longrightarrow} \text{R}_2\text{COO} \overset{-}\text{CH} + \text{CH}_3\overset{\text{O}}{\longrightarrow} \text{OCH}_3 \]

intermediet tetrahedral

\[ \text{R}_1\text{COO} \overset{\text{CH}_2}{\longrightarrow} + \text{CH}_2\overset{\text{O}}{\longrightarrow} \text{R}_3 \]

\[ \text{R}_1\text{COO} \overset{\text{CH}_2}{\longrightarrow} + \text{CH}_2\overset{\text{O}}{\longrightarrow} \text{R}_3 \overset{\text{O}}{\longrightarrow} \text{CH}_3\overset{\text{O}}{\longrightarrow} \text{OCH}_3 \]

metil ester

\[ \text{R}_1\text{COO} \overset{\text{CH}_2}{\longrightarrow} + \text{CH}_2\overset{\text{O}}{\longrightarrow} \text{R}_3 \overset{\text{O}}{\longrightarrow} \text{CH}_3\overset{\text{O}}{\longrightarrow} \text{OCH}_3 \]

digliserida

\[ \text{ion metoksida} \]
Stage 3. The Formation of Monoglycerides and Methyl Esters

\[
\begin{align*}
R_1\text{COO} - \text{CH}_2 & \quad \text{O} \quad \text{O} \\
\text{HC} & \quad \text{O} \quad \text{CR}_2 \quad + \quad \text{CH}_3\text{O} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad \text{R}_1\text{COO} - \text{CH}_2 & \quad \text{OCH}_3 \\
\text{HC} & \quad \text{O} \quad \text{CR}_2 \\
\text{H}_2\text{C} & \quad \text{OH}
\end{align*}
\]

intermedi tetrahedral

\[
\begin{align*}
R_1\text{COO} - \text{CH}_2 & \quad \text{OCH}_3 \\
\text{HC} & \quad \text{O} \quad \text{CR}_2 \quad + \quad \text{CH}_3\text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad \text{R}_1\text{COO} - \text{CH}_2 \\
\text{HC} & \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{OH}
\end{align*}
\]

methyl ester

\[
\begin{align*}
R_1\text{COO} - \text{CH}_2 \\
\text{HC} & \quad \text{O} \quad + \quad \text{CH}_3\text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad 
\end{align*}
\]

monoglyceride

Stage 4. The Formation of Glycerol and Methyl Esters

\[
\begin{align*}
\text{O} \\
R_1\text{CO} - \text{CH}_2 & \quad \text{O} \\
\text{HC} & \quad \text{OH} \quad + \quad \text{CH}_3\text{O} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad 
\end{align*}
\]

intermedi tetrahedral

\[
\begin{align*}
R_1\text{CO} - \text{CH}_2 & \quad \text{O} \\
\text{OCH}_3 & \quad \text{HC} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad 
\end{align*}
\]

metil ester

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \\
\text{HC} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad 
\end{align*}
\]

glycerol

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \\
\text{HC} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{OH} & \quad 
\end{align*}
\]

ion metoksida
The mechanism of transesterification began with the reaction between catalysts mixed with methanol to produce a methoxide group. Then, the methoxide group attacked the carbonyl C at the triglyceride molecule to form a tetrahedral intermediate that was unstable. The next step was to form methyl esters as the main product and glycerol as a by-product. In the transesterification reaction using a CaO catalyst combined with ZnO aimed to not dissolve the active phase of CaO in the reaction medium because of the strong interaction between the active side and catalyst support. Besides that, the use of CaO-ZnO catalyst could improve the basic properties of the catalyst so that the optimum level of methyl ester yield could be obtained. The physical appearance of the methyl ester synthesized can be seen in Figure 3.

In this transesterification process, the first step was to determine the optimum synthesis results based on the produced yield at different variations of CaO-ZnO catalyst concentration. Methyl ester yield from the synthesis of various concentrations of CaO-ZnO catalyst can be seen in Table 1.

![Figure 3. The results of synthesis methyl ester](image)

| Mol comparison oil : methanol | CaO-ZnO (% w/w oil) | Sample weight (g) | Theoretical weight (g) | Synthesis weight result (g) | Yield (%) | Average yield (%) |
|------------------------------|---------------------|-------------------|------------------------|---------------------------|-----------|------------------|
| 1:15                         | 3                   | 20.05             | 20.14                  | 15.57                     | 77.29     | 77.12            |
|                              | 3                   | 20.02             | 20.11                  | 15.48                     | 76.95     |                  |
|                              | 4                   | 20.05             | 20.14                  | 17.04                     | 84.58     | 84.74            |
|                              | 4                   | 20.06             | 20.15                  | 17.11                     | 84.91     |                  |
|                              | 5                   | 20.04             | 20.13                  | 15.94                     | 79.18     | 79.31            |
|                              | 5                   | 20.06             | 20.15                  | 16.01                     | 79.45     |                  |

The transesterification reaction of vegetable oil with alkaline catalyst alcohol was influenced by the amount of catalyst used [7,10]. Table 1 shows the yield of the synthesized methyl ester with a variation of the concentration of CaO-ZnO catalyst of 3%, 4%, and 5% w/w of 77.12%, 84.74%, and 79.31%, respectively. Based on these results the highest yield was obtained from CaO-ZnO catalyst concentration of 4% w/w with a yield of 84.74%.

3.5. Identification of Methyl Ester Composition with GC-MS
Identification using GC-MS was carried out to determine the components of the synthesis of methyl esters. This identification was based on the peak of the chromatogram formed [11]. The chromatogram of methyl ester synthesized by GC-MS can be seen in Figure 4. It shows that there are five main component peaks. The retention time and chromatogram peak coverage of the five main components of biodiesel which built the low-quality crude palm oil can be seen in Table 2.
Figure 4. Chromatograph GC-MS methyl ester synthesis result

| Peak | Retention time (minute) | Area       | Percent composition |
|------|-------------------------|------------|---------------------|
| 1    | 22.104                  | 6237783    | 2.72                |
| 2    | 28.279                  | 125725337  | 54.87               |
| 3    | 34.743                  | 13246852   | 5.78                |
| 4    | 34.949                  | 61477606   | 26.83               |
| 5    | 35.690                  | 5845233    | 2.55                |

Table 2. Retention time and percent composition of methyl esters

The determination of the type of methyl ester compound for each peak could be analyzed based on the peak mass spectrum of the chromatogram. For instance, the peak with a retention time (tR) of 22.104 minutes was characterized using mass spectrum chromatogram. The mass spectrum obtained was compared with the mass spectrum contained in the WILEY7.LIB Library and the fragment patterns analyzed were thought to be methyl myristate or methyl tetradecanoate compounds. Possible compounds in the form of methyl myristate or methyl tetradecanoate were strengthened by fragmentation patterns of which peaks had m/z 41, 74, 87, 143, 211, and 242. The peak with m/z 211 was thought to be derived from the breakdown of molecular ions m/z 242 as follows:

\[
\text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}_2\text{C}^{\cdot}\text{OCH}_3 \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}_2\text{C}^{\cdot}\text{OCH}_3^{+}\quad \text{m/z 242}
\]

The peak with m/z 143 was expected to be derived from the solving of molecular ions with m/z 298 as follows:

\[
\text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{CH}^{\cdot}\text{OCH}_3 \rightarrow \text{CH}_2\text{(CH}_2\text{)}_3\text{C}^{\cdot}\text{OCH}_3 + \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{C}^{\cdot}\text{OCH}_3 \quad \text{m/z 242}
\]

\[
\text{CH}_3\text{(CH}_2\text{)}_3\text{C}^{\cdot}\text{OCH}_3 + \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{C}^{\cdot}\text{OCH}_3 \rightarrow \text{CH}_3\text{(CH}_2\text{)}_3\text{C}^{+}\text{OCH}_3 + \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_2\text{C}^{\cdot}\text{OCH}_3 \quad \text{m/z 143}
\]
The peak with m/z 87 was expected to be derived from the solving of molecular ions with m/z 298 as follows:

\[
\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OCH}_3 + \text{CH}_2(\text{CH}_2)_7\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{CCH}_3\text{OCH}_3
\]

m/z 242

m/z 87

The peak with m/z 74 appearing as a base peak was thought to have been obtained from the following Mc Lafferty rearrangements:

\[
\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OCH}_3 + \text{CH}_2(\text{CH}_2)_7\text{CH}_3 \rightarrow \text{H}_2\text{C} = \text{CCH}_3\text{OCH}_3
\]

m/z 242

m/z 74

Based on chromatogram fragmentation analysis with retention times of 22.104 minutes and m/z, 74, 87, 143, and 242 it is suspected that the compound is methyl stearate.

\[
\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{C} \rightarrow \text{C} \rightarrow \text{OCH}_3
\]

methyl myristate

The mass spectroscopy fragmentation analysis of the transesterification compounds for other peaks could be carried out in the same way as methyl myristate compounds. The result of GC-MS analysis for chromatogram at the time of rent 28.279, 34.743, 34.949, and 35.690 minutes, after being matched with the existing library, it was a mixture of methyl esters. These compounds were methyl myristate (2.72%), methyl crude palmitate (54.87%), methyl linoleate (5.78%), methyl oleate (26.83%), and methyl stearate (2.55%) [12]. These results are in accordance with the theory that the highest fatty acid content in crude palm oil is crude palmitate acid.

3.6. Characterization of Methyl Esters from Synthesis

The methyl esters which have been synthesized were characterized based on SNI 7182-2015 to find out whether this methyl ester had the potential or not as biodiesel. The characterization results are presented in the following discussion.

3.6.1. Mass density

Specific mass shows the mass ratio of the volume union of a substance. The specific mass is related to the calorific value and power produced by diesel engines per unit of fuel volume. The result of determining the density of methyl esters from the synthesis results was 0.876. Based on these data, the density of methyl esters and the density of the low-quality crude palm oil were different. This indicated that the synthesis had produced a new compound in the form of methyl esters. The methyl ester mass was smaller than the low-quality crude palm oil mass. The synthesized methyl ester mass met SNI 7182-2015 biodiesel quality standards namely 0.850-0.890 g/mL so that it has the potential as biodiesel.
3.6.2. Viscosity
Table 3 shows that the viscosity of the synthesized methyl ester was 3.60 cSt. The viscosity of the synthesized methyl ester was different from the viscosity of the low-quality crude palm oil which was 25.5 cSt. This indicated that the synthesis had produced a new compound in the form of methyl esters. The viscosity of methyl esters was lower than the viscosity of the low-quality crude palm oil because it was influenced by the forces between the molecules. The viscosity of the methyl ester synthesized also met the SNI 7182-2015 biodiesel quality standard, which was 2.30-6.00 cSt. Hence, it has the potential as biodiesel.

| Experiment | Time (s) | Viscosity Methyl Ester (cSt) |
|------------|----------|------------------------------|
| 1          | 6.36     | 3.61                         |
| 2          | 6.33     | 3.59                         |
| Average    | 6.35     | 3.60                         |

3.6.3. Acid Number
Acid numbers represent the amount of milligrams of KOH needed to neutralize free fatty acids contained in 1 gram of oil or fat. The higher the acid number, the free fatty acids contained in the methyl esters produced by the synthesis. Free fatty acids that are too high can cause corrosion and damage to the machine. The acid number in the synthesized methyl ester was 0.39 mg KOH/g methyl ester. The acid number decreased because of the amount of free fatty acids that had been transesterified into new esters. The amount of the synthesized methyl ester acid met the standards of SNI 7182-2015 with a maximum value of 0.5 mg KOH/g biodiesel. This indicated that methyl esters were synthesized as potential biodiesel.

The characteristics of the obtained methyl ester syntheses were then compared with the characteristics of SNI biodiesel 7182-2015. This comparison was done to determine whether the methyl esters were synthesized as potential biodiesel. The comparison of the character of methyl esters synthesized from the low-quality crude palm oil and SNI biodiesel are listed in Table 4. It shows that the character of methyl ester synthesized from the low-quality crude palm oil using CaO-ZnO catalyst has fulfilled the character of SNI biodiesel. Therefore, it can be concluded that the synthesized methyl ester has the potential as biodiesel.

| Parameter       | Methyl Ester Result | SNI Biodiesel      |
|-----------------|---------------------|--------------------|
| Density         | 0.877 g/ml          | 0.850-0.890 g/mL   |
| Viscosity       | 3.60 cSt            | 2.30-6.00 cSt      |
| Refractive index| 1.448               | 1.3- 1.45          |
| Acidic Number   | 0.39 mg/L           | Max. 0.5 mg/L      |

4. Conclusion
From the results of the study, some conclusions can be drawn, namely methyl esters could be synthesized from a low-quality crude palm oil through a transesterification reaction using CaO-ZnO catalyst. The highest yield was obtained from the use of catalyst 4% w/w of oil with a yield of 84.74%. Components of the constituent compounds of the mixture of methyl ester synthesized were methyl myristate (2.72%), methyl crude palmitate (54.87%), methyl linoleic (5.78), methyl oleate (26.83%), and methyl stearate (2.55%), and the results of the characterization of the synthesized methyl ester showed a density of 0.876 g/mL, a viscosity of 3.60 cSt, a refractive index of 1.448, and an acid number of 0.39 mg KOH/g of methyl ester resulting in the potential methyl ester as biodiesel.
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