The Effect of K₂O Concentration in K₂O/Al₂O₃ Catalyst on Methyl Ester (Biodiesel) Synthesis from CPO Off Grade with Ultrasonic Wave

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Abstract: Fatty acid methyl esters can be made through transesterification of vegetable oils with homogeneous or heterogeneous catalysts. Ultrasonic waves and the type of catalyst affect the transesterification reaction. The purpose of this study was to determine the effect of ultrasonic waves on the transesterification of CPO with the K₂O/Al₂O₃ catalyst. Research stages: CPO off grade characterization, activation and characterization of natural zeolite, preparation and characterization of K₂O/Al₂O₃ catalysts, and oil esterification. Transesterification of CPO with K₂O/Al₂O₃ catalyst (3% w/w) at various levels of K₂O assisted by ultrasonic waves. The characterization of transesterification results includes density, viscosity, refractive index, and acid number. The use of ultrasonic waves reduces the transesterification reaction time from 120 to 35 minutes. The optimum conditions of methyl ester synthesis were achieved in the K₂O/Al₂O₃ catalyst with K₂O levels of 35% w/w, with a yield of 88.06%. Characteristics of the synthesized methyl ester include density, viscosity, refractive index, and acid number respectively are 0.891 g/mol, 7.86 cSt, 1.454 and 0.465 which are in accordance with SNI biodiesel.

1. Introduction

Energy demand always increase every year. The need for energy is still largely fulfilled from the earth's oil. Fuel from petroleum is a non-renewable energy source, so to fulfill the needs of fuel oil, energy sources alternative that can be renewed are needed [1]. Biodiesel is one of energy source alternative that is recommended as a substitute for petroleum. Biodiesel is a transesterification of long chain carboxylic acids which can be synthesized from vegetable oils or animal oils through esterification or transesterification processes. Transesterification synthesis is carried out by reacting triglycerides and alcohols assisted by acidic or basic catalysts in the process of transesterification and reacting carboxylic acids with methanol in the esterification process [2]. Triglycerides and carboxylic acids can be found in several types of vegetable oils and animal oils. Vegetable oil which is quite abundant in Indonesia is palm oil. Palm oil is divided into groups according to quality. Low quality palm oil has high levels of free fatty acids and does not meet the standards as raw material for production so that it ends up being waste. High levels of free fatty acids in low quality palm oil have the potential as a raw material in the production of biodiesel and make it possible to use this biodiesel feedstock in this research [3].
In general, biodiesel is synthesized through esterification and transesterification reactions [4]. Two things that are not considered in the transesterification process even though it affects the results of the transesterification synthesis are the stirring process and the catalyst used to accelerate the reaction rate in the synthesis process. The transesterification process usually used a homogeneous catalyst such as a KOH or NaOH solution [5]. The use of homogeneous catalysts has a disadvantage, which is very difficult to separate from the product because it has the same phase. The process of separating the catalyst from the product requires a lot of water in its purification so that the waste water from biodiesel purification can be corrosive and pollute the environment [6] Homogeneous catalyst with carboxylic acids will form alkaline soap and water which can reduce the quality of transesterification produced. Alkaline soap and water formed in the transesterification process can be minimized with heterogeneous catalysts in this study. Heterogeneous catalysts have several advantages including being easily separated, minimizing the formation of water and alkaline soap, resistant to high temperatures, and not corrosive [7].

The heterogeneous catalyst that has been developed at the moment is the heterogeneous catalyst K₂O/Al₂O₃, which is a solid compound that can increase the strength of the base [8] so it can be functioned as a good catalyst support in the transesterification reaction. This study includes the impregnation of KOH into Al₂O₃ then calcined at high temperature into a heterogeneous catalyst K₂O/Al₂O₃ and can produce 96.8% transesterification yield [9].

The oil, catalyst and alcohol in the transesterification reaction can not mixed well, so it needs the energy to help the mixing process. Biodiesel synthesis is generally carried out with mechanical stirrers. The stirring is less optimal and requires a long time. In this study the stirring process was assisted by ultrasonic waves thereby reducing reaction time [10][11]. Ultrasonic waves have a high intensity or frequency, causing small bubbles on the liquid media. When the maximal pressure of bubble approaches, the bubble experiences a split called cavitation [12]. Cavitation produced by ultrasonic waves can help the reaction between triglycerides with alcohol in the formation of alkyl esters. The yield of transesterification results using ultrasonic waves is higher than using conventional stirring. Based on this background, the propose of this research is transesterification of low quality palm oil with K₂O/Al₂O₃ catalysts and ultrasonic waves [9].

2. Method

This research is a type of laboratory experimental research. This research went through several stages, such as characterization of low quality palm oil, activation and characterization of natural zeolite, preparation and characterization of K₂O/Al₂O₃ catalysts, Raffination low quality palm oil, determination of free fatty acid levels of refined palm oil resulting from K₂O/Al₂O₃ refined palm oil rafination, transesterification of esterified palm oil with K₂O/Al₂O₃ catalyst with the help of ultrasonic waves, and characterization of transesterification results include density, viscosity, refractive index, and acid number.

2.1. Tools and Material

The tools used in this research are beaker, burette, static glass, clamps, fillers, measuring flasks, analytical balance with 0.01 gram accuracy, glass bottles, spray bottles, dropper pipettes, volume pipettes, Erlenmeyer, porcelain plates, crucible, separating funnel, three-neck flask, 100 °C thermometer, glass funnel, watch glass, mortar and pestle, stir bar, spatula, universal indicator paper, filter paper, warp plastic, warp paper, label paper, aluminum foil, a set of reflexes, a set of ultrasonic wave instruments, a set of Buchner tools, centrifuges, hot plate and magnetic stirrer, furnaces, ovens, 100 mesh size sieves, Abbe refractors, Ostwald Viscometers, SEM-EDX instruments, XRF instruments, XRD instruments and GC-MS instruments.

The materials used in this study are natural mordenite zeolite obtained from south Malang, low quality palm oil (CPO off grade) from Lodoyo Blitar, methanol, ethanol, 37% HCl, MgSO₄ anhydrous, indicator of phenolphthalein, KOH, Al₂O₃ powder, and distilled water.
2.2. Characterization of low-quality palm oil
Low quality palm oil obtained from PT. Sawit Arum Madani in Sutojayan Blitar Indonesia. Characterization of low-quality palm oil includes density, refractive index, viscosity, and free fatty acid levels.

2.3. Synthesis and characterization of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst in various percent of $\text{K}_2\text{O}$ catalyst
$\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst is made by wet impregnation method. Potassium hydroxide solids were dissolved with distilled water and then $\text{Al}_2\text{O}_3$ solids was added with various ratio of KOH : $\text{Al}_2\text{O}_3$ as follows 15:85, 20:80, 25:75, 30:70. Each mixture of KOH and $\text{Al}_2\text{O}_3$ was stirred for 3 hours then roasted for 24 hours at 110 °C, then calcined at 500 °C for 3 hours [4], [13]. Preparation of $\text{Al}_2\text{O}_3$ catalysts was characterized by XRD and SEM-EDX to determine the morphology of the catalyst topography, and whether $\text{K}_2\text{O}$ was formed.

2.4. Refinement Low Quality Palm Oil
The refinement of low quality palm oil in this study aims to fade the color, remove the impurities and reduce the odors. Refination is carried out by heating the low quality palm oil at 175 °C then added with natural zeolite which has been activated as much as 2% (w/w) and stirring using a magnetic stirrer for 1 hour. The oil which has been finished with activated natural zeolite is separated by centrifuge for 15 minutes at 3000 rpm.

2.5. Esterification Palm Oil from Refination result
The esterification process in this study was to convert free fatty acids into transesterification. Fifty g of refined low quality palm oil is put into a triple neck flask that has been strung together with reflux and magnetic stirrer. The oil is heated to 40 °C, then methanol is added in a mole ratio of oil: mole of methanol (1:12), added $\text{H}_2\text{SO}_4$ 1% w/w and stirred for 3 hours at 60 °C. The mixture formed is transferred into a separating funnel and allowed to stand for 4 hours to form 2 layers [7][14].

2.6. Transesterification of Palm Oil with $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst
The transesterification process in this study aims to convert triglycerides into transesterification. Twenty g of low quality palm oil produced by esterification was put into a three neck flask and heated at 60 °C, methanol was added with a mole ratio of oil: mole of methanol (1:12) and added with 3% w / w of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst. The $\text{K}_2\text{O}$ content in the catalyst varies from 15%, 20%, 25% and 30% w/w. The variations of the mixture included ultrasonic wave reactors with various stirring time ratios of 25 minutes, 35 minutes and 50 minutes.

3. Result and Discussion

3.1. Refination Palm Oil with Activated Natural Zeolite
Refination is carried out using activated natural zeolites. The characterization of palm oil before being transformed and after finalization was carried out in this study to see the differences that occur in oil. Low quality palm oil used in this study has two integrated phases, namely the solid phase and the liquid phase. The refining process in this study was carried out by heating up to 175 °C to liquefy the solid quality low-quality palm oil to be more homogeneous. Warming up to 175 °C with stirring is able to remove the water content found in the oil sample. Furthermore, natural zeolite which has been activated as much as 2% by weight of the refined oil is added. Activated zeolite is able to absorb impurities contained in palm oil and absorb natural dyes present in palm oil so that the color changes occur before and after refining. Color changes in low quality palm oil can be seen in Figure 1.
Table 1. Characterization Results of Low-Quality Palm Oil.

| Parameter       | Value before | After rafinations |
|-----------------|--------------|-------------------|
| Density (g/mL)  | 0.918        | 0.919             |
| Viscosity (cSt) | 25.90        | 25.90             |
| Refractive index| 1.463        | 1.463             |

Figure 1. Palm oil (a) before rafination and (b) after rafination.

3.2. Esterification Palm Oil from Rafination Result

Transesterification of low quality palm oil contains high free fatty acid content for example 10.92%, must be carried out in two stages, started with esterification. The purpose of the esterification reaction is to convert free fatty acids into alkyl esters, so the free fatty acids do not become soap during the transesterification reaction process. The reaction of the accumulation of free fatty acids into unwanted soaps in the transesterification reaction process is as follows:

\[ \text{RCOOH} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{R'}\text{OH} \]

The transesterification process can be carried out if the free fatty acids found in low quality palm oil samples are less than 2%. The esterification process in this study was carried out by using 1% w/w H$_2$SO$_4$ catalyst and methanol. Methanol is used because it has the shortest chain so that it has a higher reactivity than other types of alcohol. High methanol reactivity makes it easy for acid catalysts to polarize methanol. The general esterification reaction is as follows [15]

\[ \text{RCOOH} + \text{CH}_3\text{OH} \rightarrow \text{RCOOCH}_3 + \text{H}_2\text{O} \]

The reaction that occurs is a reversible reaction that requires the addition of one of the reactants in excess, so the reaction goes to the product. This study uses a 1 mole ratio of oil mole: alcohol. The results of the esterification were tested for free fatty acid levels. The transesterification reaction process is then carried out if the result is less than 2%. The levels of free fatty acids resulting from esterification can be seen in Table 2.

Table 2. Esterification of Free Fatty Acid (FFA) Levels.

| Number | sample (g) | FFA (%) |
|--------|------------|---------|
| 1      | 1.049      | 1.646   |
| 2      | 1.044      | 1.182   |
| Average|            | 1.414   |

In this study, the rafination results of the esterification reaction can convert the free fatty acids contained in low-quality palm oil from 10.92% to 1.41%. The mechanism of the esterification reaction converts fatty acids into transesterification are shown in Figure 2.
3.3. Synthesis of K$_2$O/Al$_2$O$_3$ Heterogeneous Catalysts at various levels of K$_2$O

Heterogeneous catalyst used in this study was KOH impregnated into Al$_2$O$_3$. Calcination is carried out [16] until KOH decomposes to K$_2$O by heating at 500 °C for 3 hours which serves to decompose KOH into K$_2$O in the pore Al$_2$O$_3$ with the following reaction.

\[ 2\text{KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \]

The catalyst preparation results in various K$_2$O/Al$_2$O$_3$ mass ratios are shown in Figure 3. In Figure 4 the XRD of 15% K$_2$O and 20% K$_2$O catalysts showed the typical peaks with K$_2$O compounds at 2θ = 31, 39, 51, 55, 62. The XRD results are in accordance with the XRD results of the K$_2$O compound from the K$_2$O/Al$_2$O$_3$ catalyst. The results of XRD K$_2$O/Al$_2$O$_3$ characterization with 15% K$_2$O and 20% K$_2$O levels can be seen in Figures 4 and 5.
The morphological and topological structure of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ with a bar scale of 100 $\mu$m with a magnification of $1,000 \times$ is shown in Figure 5.

![Image](a)

![Image](b)

**Figure 5.** The structure of XRD $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst with (a) 15% $\text{K}_2\text{O}$ and (b) 20% $\text{K}_2\text{O}$.

Comparison of morphological and topological structure sizes with a 20 $\mu$m bar scale with magnification of $5,000 \times$ is shown in Figure 6.

![Image](a)

![Image](b)

**Figure 6.** Catalyst particle size with (a) 15% $\text{K}_2\text{O}$ fraction and (b) 20% $\text{K}_2\text{O}$ fraction.

Figure 5 and Figure 6 show the morphology and topography of the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst with variations in $\text{K}_2\text{O}$ levels of 15% and 20%. Figure 5a and Figure 6a are $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst with 15% $\text{K}_2\text{O}$ content and Figure 5b and Figure 6b are $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst with 20% $\text{K}_2\text{O}$ content. As shown in Figure 6, the catalyst size at 15% $\text{K}_2\text{O}$ fraction is between 3.129-21.460 $\mu$m with an average of 8.824 $\mu$m and at a fraction of 20 percent 2.434-14.901 $\mu$m with an average of 6.88 $\mu$m.

### 3.4. Transesterification Using $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ Catalysts with Ultrasonic Waves

This study was conducted to determine the effect of heterogeneous catalyst $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ and the effect of time variations on yield using ultrasonic waves. In this study, 20%, 25%, 30% of $\text{K}_2\text{O}$ variations of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst and reaction time of 25 minutes, 35 minutes, and 50 minutes were used. Ultrasonic waves have a high intensity so that when liquid medium propagates, it will produce alternating pressure which causes small bubbles in the liquid media. At maximum bubble pressure, bubbles undergo a split called cavitation [17]. Cavitation generated by ultrasonic waves can help the reaction process between triglycerides and alcohol in the transesterification reaction. The series of processing tools for the transesterification process using ultrasonic waves is shown in Figure 7.
Figure 7. Series of Transesterification Process Tools Using Ultrasonic Waves.

The yield of transesterification results from low quality palm oil using heterogeneous catalyst K$_2$O/Al$_2$O$_3$ in various mass ratio assisted with ultrasonic waves at time variations can be seen in Figure 8.

![Graphs of yield vs time for transesterification with different catalyst contents](image)

Figure 8. Result of transesterification results with K$_2$O/Al$_2$O$_3$ catalyst with (a) 15% content, (b) 20% content, (c) 25% content, and (c) 30% content of K$_2$O to Reaction time variations.

Figure 8a and Figure 8b show with the increasing time, the percentage of reaction results tends to decrease. Transesterification with 15% and 20% K$_2$O catalysts was suspected to undergo a saponification reaction, thereby reducing the reaction results. Figure 8c and Figure 8d show the results of transesterification using heterogeneous catalyst K$_2$O/Al$_2$O$_3$ with the help of ultrasonic waves at various time variations have increased. The increasing of yield indicates the longer time needed for the
transesterification process at 25% K_2O levels on heterogeneous K_2O/Al_2O_3 catalysts. The smaller the saponification reaction increases the transesterification result. Fig. 12 shows the yield of transesterification using heterogeneous catalyst K_2O/Al_2O_3 with the help of ultrasonic waves at various time variations that have increased and then decreased. The three-time variations result experienced the highest yield compared to other catalyst variations. Increasing and decreasing results indicate the longer time required for the transesterification process at 30% K_2O levels on heterogeneous catalyst K_2O/Al_2O_3 experiences low lathering reactions so that the resulting transesterification increases compared to other catalyst variations.

3.5. Characterization of Transesterification Results
The characterization results of low-quality palm oil transesterification with the K_2O/Al_2O_3 catalyst with ultrasonic waves as in Table 3. As shown in Table 3, the results of low-quality palm oil transesterification with K_2O/Al_2O_3 catalyst with ultrasonic waves have characteristics that are close to SNI Biodiesel 2015. This is in accordance with Santoso 2019 that the results of the synthesis of methyl ester with K_2O/Al_2O_3 catalyst products are in accordance with SNI biodiesel.

| Table 3. Results of Transesterification Characterization. |
|----------------------------------------------------------|
| Parameter | Results Transesterification | SNI Biodiesel |
| Density (g/mL) | 0.891 | 0.85-0.89 |
| Viscosity (cSt) | 7.86 | 2.3-6.0 |
| Free Fatty acid (mg KOH/g) | 0.465 | Maks 0.5 |
| Refractive index | 1.454 | 1.3-1.4 |

4. Conclusions
Synthesis of K_2O/Al_2O_3 can be carried out by the wet impregnation method of KOH and Al_2O_3 then calcined at a high temperature of 300 °C for 3 hours. The XRD results an angle of 10-90 ° at 2θ = 31, 39, 51, 55 and 62 which are the typical peaks of the K_2O compound. The yield of transesterification results is influenced by the K_2O content in the catalyst. The optimum conditions of the reaction are achieved at 30% K_2O levels in the K_2O/Al_2O_3 catalyst with 35 minutes of reaction time. The yield of K_2O/Al_2O_3 obtained 88.06% (w/w). The characterization result of transesterification has a density of 0.891 g/mol, a viscosity of 7.86 cSt, a refractive index of 1.454 and an acid number of 0.465 and showed the potential as biodiesel.

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