Methyl Ester Synthesis of Crude Palm Oil Off Grade Using the K$_2$O/Al$_2$O$_3$ Catalyst and Its Potential as Biodiesel

Aman Santoso*, Sumari, Urfa Zakiyya U, Tiara Nur A
Department of Chemistry, Faculty of Mathematics and Natural Sciences, State University of Malang, Jl. Semarang No. 5 Malang, 65145, Indonesia

*Corresponding author’s email: aman.santoso.fmipa@um.ac.id

Abstract: The purpose of this research was to synthesize the methyl ester of crude palm oil off grade using a K$_2$O/Al$_2$O$_3$ catalyst and its potential as a biodiesel. The procedure of this study was refining CPO off grade using active natural zeolite, CPO off grade of esterification, transesterification of CPO off grade using a K$_2$O/Al$_2$O$_3$ catalyst by varying the concentrations of 2~4% (w/w) catalyst. The results showed that the activation of natural zeolite HCl 2% (w/w) could be used for refining CPO off grade; the methyl ester could be synthesized from CPO off grade through transesterification of K$_2$O/Al$_2$O$_3$ catalyst that obtained the highest yield of 85.58% (w/w) at the catalyst concentration of 4% (w/w). The results of catalyst characterization of methyl ester with 4% (w/w) of methyl esters obtained a density of 0.86 g/mL, a viscosity of 4.33 cSt, a refractive index of 1.45, and the acid number of 0.49 mg/g methyl ester thus fulfilling SNI biodiesel; the major components of the building blocks of the methyl ester transesterification catalyst results of K$_2$O/Al$_2$O$_3$ were methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate.

Keywords: Methyl ester, palm oil off grade, heterogeneous catalyst, biodiesel

1. Introduction
Fuel oil is the main energy source used in various countries including Indonesia. The sustainable use of fossil energy will reduce oil reserves and improve air pollution. It encourages the development of alternative renewable energy which is environmentally friendly; one of which is biodiesel. Biodiesel is a methyl ester of long-chain compounds that can be produced through a transesterification process of animal’s fat or vegetable oil such as crude palm oil (CPO) [1,2], and because its availability is quite abundant in Indonesia.

The increased production of CPO by industries in Indonesia is followed by the increased production of CPO off grade. CPO off grade is of inferior quality of CPO characterized by high free fatty acid content of more than 5%. CPO off grade generally has a dark red color, pungent, and contains gum so it needs a refining to improve the quality. The refined process typically uses such as natural zeolite adsorbent. Natural zeolite is selected as an adsorbent because it is relatively cheap and plentiful, and has many pores so that it has a high adsorption capability. Before being used as an adsorbent in a refined process, natural zeolites need to be activated and modified first to increase the adsorption power.

The high cost of biodiesel production from vegetable oils gives more advantages for the development of CPO off grade as an alternative raw material because they are relatively cheaper. Biodiesel production
is influenced by several important factors of catalyst. Homogeneous catalysts have some weaknesses that require a purification process that is quite difficult because the catalyst and the reaction products are in the same phase as liquid, corrosive, and catalysts that cannot be reused will be ultimately discarded as wastewater which can pollute the environment [3]. Today, the heterogeneous catalysts were developed to solve these weaknesses. The heterogeneous catalysts have the advantages such as low corrosivity nature, easily separated from the product, reusable, and more environmentally friendly [4]. One of the heterogeneous catalysts that have been used for the synthesis of biodiesel is a strong base KOH catalyst impregnated in Al₂O₃. The process of making biodiesel through transesterification reaction of *nyamplung* oil using KOH/Al₂O₃ catalysts achieved optimum conditions using KOH comparison: Al₂O₃ is 1 : 3. This reaction was carried out at a temperature of 65 °C, the percentage of optimum catalysts used as much as 3%; the mole ratio of oil/methanol was 1:10; and the yield of methyl ester obtained was 90%.

This study used a base heterogeneous catalyst of K₂O/Al₂O₃; this was made from KOH supported by alumina. Potassium hydroxide that supported was selected as a catalyst for a strong base group including alkali. The alkalinity of the alkali oxides is stronger than the alkaline earth oxides and oxides of transition. Potassium hydroxide catalyst in the industry is often used as a homogeneous catalyst. However, the process of KOH catalyst separation from the reaction products was difficult which resulted in the decreasing yield of methyl ester and rising production costs. Therefore, the KOH modified into a heterogeneous catalyst was impregnated into the support such as Al₂O₃. Alumina is widely used as a support for producing biodiesel because it has a high porosity, mechanical and thermal stability for esterification and transesterification reactions [5,6]. Additionally, the impregnation of KOH in Al₂O₃ catalysts for alkalinity increased, so the catalytic activity increased.

2. Methods

2.1. Tools and Materials
The tools used in the research were 50 mL beaker (Iwaki), 400 mL beaker (pyrex), measuring cups of 25 mL and 5 mL (Iwaki), 10 mL burettes (duran), 50 mL burettes (pyrex), static, clamps, filler, flask of 100, 200, and 500 mL (Iwaki), analytical balance to the nearest 0.01 gram (And HF-3000), glass bottles, spray bottles, pipette, pipette volume of 25 mL and 1 mL (Eterna), 100 and 250 mL Erlenmeyer (Iwaki), porcelain dish, Crucible, 10 mL funnel (Iwaki), three neck flask of 300 mL (Iwaki), 100 °C thermometer, funnel glass, watch glass, mortar and PESTEL, stir bar, spatula, paper universal indicator (Brand), filter paper, plastic wrap, label paper, aluminum foil, desiccator, a set of tools reflux, a set of Buchner, centrifuged (H-103n KOKUSAN), hot plate and magnetic stirrer (HMS-79), furnace (Thermolyne), oven (Memmert), a sieve size of 50 mesh, Abbe refractometer, Ostwald viscometer, XRD (PANalytical Xpert -Pro), XRF (Pananalytical MiniPal 4) spectroscopy, and GC–MS (Shimadzu QP2010 Plus).

The materials used in the research were natural zeolite mordenite obtained from Source Manjing Wetan, Malang. The crude palm oil (CPO) off grade was obtained from PT. Arum Palm Madani Sutojayan, Blitar, Methanol Pa 95%, ethanol, HCl 37% pa, Oxalic Acid dihydrate pa, phenolphthalein indicator, KOH pa, pa Al₂O₃ powder (Merck), n-hexane pa, pa diethyl ether, acetic acid pa, and iodine pa.

2.2. Preparation of Activated Zeolite HCl.
Natural zeolite is clean and dry which was ground with a mortar until smooth, then sieved to 50 mesh size. The zeolite was washed with distilled water and filtered with a Buchner funnel and dried at 105 °C. That zeolite was added with 3 M HCl while being stirred for 3 hours. The zeolite was filtered and neutralized using distilled water until the pH range of 6–7. The zeolite was roasted at 105 °C for 2 hours and in-furnace at 300 °C [7], the zeolite before and after activation HCl was characterized using X–Ray Fluorescence (XRF).
2.3. Refining CPO off Grade Activated Zeolite Using HCl
CPO off grade was refined to reduce the color, odor, and the levels of free fatty acids. The refinement was conducted by CPO off grade plus 2% (w/w) activated zeolite 3 M HCl. It was then heated at 170 °C while being stirred using a magnetic stirrer for 1 hour. The results of CPO off grade refinement was then centrifuged for 20 minutes at 3,000 rpm. The characterization of CPO off grade refined results was done with two parameters based on the physical properties (color and odor) and chemical properties (determination of free fatty acid).

2.4. Catalyst Preparation K$_2$O/Al$_2$O$_3$
The preparation of K$_2$O/Al$_2$O$_3$ catalyst was carried out with the impregnation method, mixing KOH solution with a solid Al$_2$O$_3$. The KOH solution was poured in a glass beaker, and mixed with Al$_2$O$_3$ with a mass ratio of 1:3. The mixture was then stirred using the magnetic stirrer for 3 hours at room temperature. Subsequently, the mixture was dried in an oven at 110 °C for 24 hours. The dry KOH/Al$_2$O$_3$ mixture was crushed with a mortar, and then calcined in a furnace at 300 °C for 2 hours. The synthesis results were characterized using X−Ray Diffraction (XRD) [8].

2.5. CPO Esterification Using H$_2$SO$_4$
A total of 50.0287 grams of refined palm oil off grade results was put in a three-neck flask strung with reflux and magnetic stirrer. Methanol with a mole ratio of oil of 1:12 was added then heated for 3 hours at a constant temperature of 60 °C. The mixture was then transferred to a separating funnel and allowed to stand for 24 hours to form two layers. Both layers were separated and the bottom layer was washed with warm water in a separated funnel. Then, the bottom layer was separated from water and heated to a temperature of 90−100 °C to evaporate the residual water washing. Subsequently, anhydrous MgSO$_4$ was added and decanted to separate solids anhydrous MgSO$_4$. After that, the levels of free fatty acids were tested [9].

2.6. Transesterification CPO Grade off with K$_2$O/Al$_2$O$_3$ Catalyst
The synthesis of methyl ester via transesterification with heterogeneous catalysts of K$_2$O/Al$_2$O$_3$ was done by weighing 20.017 g CPO off grade of esterification results then introduced into the three-neck flask and heated at 60 °C. Once the temperature reached 60 °C, a mixture of methanol with a mole ratio of oil of 1:12, methanol and catalyst K$_2$O/Al$_2$O$_3$ with the variation of the concentrations of 2%; 3%; 4% (w/w) was added. The mixture was stirred at reflux for 4 at 300 rpm. The mixture was centrifuged at 3,000 rpm for 20 minutes. Then, the mixture was put in a separated funnel and allowed to stand for 24 hours. After that, two layers would be formed; the top layer was suspected of methyl ester and glycerol allegedly undercoat. The top layer was washed with warm water and let stand in a separated funnel to form two layers. Then, methyl ester was separated from the water and heated to a temperature of 90 − 100 °C to evaporate the residual water washing. Furthermore, anhydrous MgSO$_4$ was added and decanted to separate solids anhydrous MgSO$_4$. The identification and characterization of methyl ester synthesis results included TLC test, the density, viscosity, acid number, refractive index, and the identification of GC−MS.

3. Results and Discussion

3.1. Characterization of Zeolite
Natural zeolites were activated physically and chemically. The physical activation was done by crushing and sieving 50 mesh which aimed to unify and expand the size of the zeolite surface so that the zeolite adsorption ability increased. The chemical activation was undertaken by adding HCl that caused dealumination of zeolites. Dealumination caused the decrease in the levels of Al from the structure of the zeolite that caused the rise of the ratio of Si/Al [7]. The activation of the acid led to reduce metal impurity that covered pore−zeolite pores, could increase the surface area of zeolite. The increasing
surface area resulted in an increasing adsorption process. The XRF characterization results showed Si/Al ratio of the activated natural zeolite HCl that increased as shown in Table 1.

| Samples                | Si  | Al  | The ratio of Si/Al |
|------------------------|-----|-----|-------------------|
| Natural zeolite        | 55.4| 7.0 | 7.62              |
| Activated zeolite      | 61.4| 6.2 | 9.52              |

The increase in the ratio of Si/Al caused zeolites more hydrophobic [7], [10]. The zeolite would be easier to interact with nonpolar molecules like oil in accordance with the law like dissolve like and suitable to be used as an adsorbent in CPO off grade.

3.2. Refining CPO off Grade Using Activated Zeolite

The characterization of Crude Palm Oil off grade was performed before refining stage to determine the physicochemical properties and quality of the CPO. The results of the characterization of CPO off grade are shown in Table 2.

| Parameter               | Value |
|------------------------|-------|
| Mass density (g / mL)  | 0.95  |
| Viscosity (cSt)        | 25.47 |
| The refractive index   | 1.46  |
| Free fatty acid content (%) | 8.50 |

Table 2 shows that the value of the density, viscosity, refractive index, and free fatty acids was quite high CPO. Free fatty acid content was high (> 5%); it showed the used inferior quality of CPO (off grade) so that the process of refining was necessary [11]. The refinement was done using the activated natural zeolite HCl 2% (w/w) which aimed to reduce color, odor, organic compounds that were not desirable, and lower levels of free fatty acids. The CPO off grade has refined the changing color from dark red to orange. The dye in the CPO off grade was absorbed by the surf

3.3. Esterification of CPO off Grade

The process of making biodiesel oils containing high free fatty acid more than 2% preferably used a two-stage process, namely the esterification, followed by a transesterification process. Esterification process using acid catalysts aimed to reduce the levels of free fatty acids to less than 2% [13]. The CPO off grade containing high free fatty acids was likely to cause soap when it was directly [14]. Esterification produces methyl ester and water. The results of the synthesis of methyl ester were included into the funnel and formed two layers. Then, it was checked by adding approximately 25 mL water and the increasing volume layer was observed. The top layer was considered to be water, alcohol remainder of the reaction, and the acid catalyst (the layer increase in volume), while the bottom layer was assumed to be a mixture of triglycerides and the methyl esters. The esterification process could reduce free fatty acid content of less than 2%, amounting to 0.7%. The decreasing levels of free fatty acids due in part to free fatty acids have been converted into methyl esters.

3.4. Characterization K_2O/Al_2O_3 Catalysts

The catalyst used in this study was a heterogeneous catalyst of KOH alkaline alkali impregnated into Al_2O_3. Alumina can be used as a catalyst support by extending the active core surface of the base to the entire surface [15]. KOH acted as the active core component that could be impregnated into the porous support material such as alumina. The aim was to improve the impregnation of the active side (alkalinity
catalyst) and disperse evenly across the surface of the support. Hydroxyl group was active on the alumina side. Impregnation caused the protons in the hydroxyl groups replaced with K$^+$ ions to form Al–O–K. The density of hydroxyl groups increased with the number of protons of hydroxyl groups which could be replaced by K$^+$, it was directly proportional to the increase in the activity of the catalyst [16]. The K$_2$O/Al$_2$O$_3$ catalyst has been impregnated white. The calcination caused KOH to turn into K$_2$O due to decomposition. Subsequently, the synthesized catalysts were characterized using XRD to determine the success of K$_2$O/Al$_2$O$_3$ catalyst preparation shown in Figure 1.

![X-ray diffraction pattern of the sample](image)

**Figure 1.** X-ray diffraction pattern of the sample

Figure 1 shows that the K$_2$O/Al$_2$O$_3$ catalyst has been successfully synthesized marked by the emergence of K$_2$O peak at an angle of $2\theta = 32.22^\circ$ (JCPDS 47–1701) indicating that the KOH contained in the Al$_2$O$_3$ turned into K$_2$O after calcination. Meanwhile, the peak at an angle of $2\theta = 67.10$ (JCPDS 10–173) indicated Al$_2$O$_3$.

### 3.5 Transesterification using K$_2$O/Al$_2$O$_3$ catalyst

CPO off grade after passing the stage of esterification, free fatty acid levels fell to 0.7% to proceed to the stage of transesterification. Methyl ester synthesis was conducted by reacting CPO off grade with a mixture of K$_2$O / Al$_2$O$_3$ methanol–catalyst which was then refluxed [17]. The reaction temperature used in the synthesis was 60 °C so that the methanol did not evaporate because the boiling point of methanol was 64.5 °C (MSDS). The results obtained methyl ester synthesis centrifuged to separate from the solid catalyst after it was put into a separated funnel. After the mixture was separated to form two layers, the top layer was a methyl ester, while the bottom layer was a residual glycerol and methanol. Glycerol was located in the bottom layer because it had a density greater than the methyl ester [18]. The methyl ester was synthesized and then tested by thin layer chromatography (TLC) to ensure the formation of methyl esters. TLC test results are shown in Figure 2.
Figure 2. TLC methyl ester synthesis

TLC test used eluent n-hexane–diethyl ether–acetic acid n-hexane nonpolar immiscible with diethyl ether because of the presence of ethyl which is also nonpolar. While n-hexane was mixed with acetic acid because their nonpolar side of acetic acid was CH3–. TLC test results in Figure 2 show the formation of two different stains either on the synthesis of methyl ester with a catalyst concentration of 2% (w/w), 3% (w/w), or 4% (w/w).

Oil stains have different Rf with stains methyl ester in various concentrations of the catalyst. Rf oil stains had Rf 0.35 while methyl ester with a catalyst concentration of 2%, 3%, 4% (w/w) respectively was 0.78, 0.80, and 0.82. The stains on the top indicated a mixture of methyl ester synthesis product. The stationary phase was silica gel TLC polar phase while the silence was dominated by n-hexane nonpolar. The oil stains were below showing that the oil adsorbed by the stationary phase was polar. Meanwhile, the methyl ester was eluted by the eluent dominated by n-hexane nonpolar. The law like dissolve like methyl esters were more polar than oil. The yields of methyl ester were obtained at a concentration of 2%, 3%, and 4% (w/w), respectively were 54.90%, 73.93%, and 85.58%. The highest yield of methyl ester was at a concentration of 4% catalyst.

3.6. Methyl ester synthesis characterization results
The characterization of methyl esters included the density, viscosity, refractive index, and the acid number. The characterization results were then compared with the methyl ester Biodiesel SNI 7182–2015. The data from the methyl ester used the characterization of K2O/Al2O3 catalyst at a concentration of 2%, 3%, and 4% (w/w) as shown in Table 3.

Table 3 shows that the methyl ester synthesis of K2O/Al2O3 catalyst concentration result 2% (w/w) was only viscosity that fulfilled ISO Biodiesel 2015. The methyl ester product synthesis with a catalyst concentration of 3% (w/w) parameter of density, viscosity, and the refractive index Biodiesel met ISO 2015 while the methyl ester synthesis product with a catalyst concentration of 4% (w/w) fourth parameter Biodiesel fulfilled the standard of ISO 2015.

The density of the high CPO off grade may fall through transesterification but only the methyl esters were synthesized using a K2O/Al2O3 catalyst 3% and 4% (w/w) that fulfilled the quality standard of ISO Biodiesel 2015. The density of the methyl ester measurement results was smaller than CPO off grade because the density of the methyl ester molecule was smaller than the CPO off grade which had a smaller density. Meanwhile, the density of methyl esters used the K2O/Al2O3 catalyst 2% (w/w) that exceeded the standard of ISO 2015 Biodiesel. The density of methyl ester that exceeded the provisions would result in an incomplete combustion reaction that would cause emissions and engine wear [19].
Table 3. The results characterization of methyl ester synthesis results

| Parameter                  | Biodiesel SNI 2015 | Methyl ester synthesis result catalyst concentration K₂O / Al₂O₃ |
|---------------------------|-------------------|-----------------------------------------------------------------|
|                           | Mass density (g / mL) | CPO off grade 2% 3% 4% | Al₂O₃                                             |
|                           | 0.85 – 0.89        | 0.95 0.91 0.89         | 0.86                                              |
| Viscosity (cSt)           | 2.3 – 6.0          | 25.47 5.34 4.33        | 3.61                                              |
| Refractive index          | 1.3 –1.45          | 1.46 1.46 1.45         | 1.45                                              |
| Acid number (mg /g)       | Max. 0.5           | - 0.78 0.58            | 0.78                                              |
| Potential as a biodiesel  | -                 | - -                   | Potentially                                       |

The viscosity value of CPO off grade with high viscosity was down after going through transesterification stage. The results of the viscosity measurements were smaller than a methyl ester CPO off grade for intermolecular forces which were smaller than the methyl ester CPO off grade, causing a small viscosity. The synthesis of methyl esters used K₂O/Al₂O₃ catalysts of 2%, 3%, and 4% (w/w) that fulfilled the standard of ISO 2015 Biodiesel. The higher concentration of K₂O/Al₂O₃ catalyst used brought about the smaller viscosity value. The higher viscosity the diesel fuel, the viscosity of the fuel was also bigger causing difficult to flow.

The refractive index of CPO off grade and methyl ester with a K₂O/Al₂O₃ catalyst concentration of 2% (w/w) did not fulfill ISO 2015 Biodiesel standard. Methyl esters were synthesized using a K₂O/Al₂O₃ catalyst of 3% and 4% (w/w) to fulfill SNI 2015 biodiesel standard. The use of the K₂O/Al₂O₃ catalyst with a concentration of 2% (w/w) was suspected to be the majority of oil that had not been converted into methyl ester resulting in a great density and the distance between small molecules. If the distance between the small molecules then the velocity of light in the liquid became smaller, the refractive index became larger, and vice versa.

The greater the concentration of the catalyst used in the synthesis, the value of the acid number was getting smaller. The methyl ester used the K₂O/Al₂O₃ catalyst synthesized in amount of 4% (w/w) that fulfilled the ISO 2015 Biodiesel standard. It was possible if the catalysts with the low concentration was not sufficient to convert the free fatty acids into methyl ester, thus causing the acid number value tended to be high.

3.7 Identification GC−MS Results Synthesis of Methyl Ester CPO off Grade

GC analysis−MS showed some peaks−each peak retention time showed the compound−of the building blocks of the methyl ester. The identification of the compound was determined based on the molecular weight and fragmentation pattern of each component of methyl ester. The chromatogram of methyl ester synthesis result is presented in Figure 3.

![Chromatogram–MS Methyl Ester Synthesis by K₂O/Al₂O₃ Catalyst](image)
Figure 3 shows that in the chromatogram, there were four main compound building blocks of methyl ester, where the fourth consecutive peak with a retention time ($t_R$) of 28.199 min, 34.733 min, 34.923 min and 35.693 min existed. The mass spectral fragmentation patterns of each of the components of the methyl ester synthesis results were then analyzed. An example of the mass spectrum of the methyl ester of CPO off grade with a retention time 28.199 min is shown in Figure 4.

![Figure 4. Methyl Ester mass spectrum with a retention time (tR) of 28.199 minutes](image)

The mass spectrum in Figure 4 was then compared to mass spectral libraries listed in WILEY8.LIB then analyzed by the pattern alleged fragmentation and the compound was methyl palmitate or methyl hexadecanoate. Therefore, the pattern of the spectrum of GC-MS analysis of the chromatogram peaks would otherwise be determined by methyl ester off grade constituent of palm oil. The percentage of methyl ester produced was equivalent to the amount of area in the chromatogram. The results of the retention time and the area of the chromatogram are summarized in Table 4. Table 4 shows that the methyl ester synthesis resulted in CPO off grade with the highest levels of methyl palmitate of 48.64% and that of methyl oleate of 40.90%. This is consistent with the literature by Bahadi et al. stating that the fatty acid content of the highest grade CPO off is palmitic acid and oleic acid [20].

| Peak | Retention time (minute) | Components of methyl ester | The area (levels)% |
|------|-------------------------|----------------------------|-------------------|
| 1    | 28.199                  | methyl palmitate           | 49.64             |
| 2    | 34.733                  | methyl linoleate           | 5.52              |
| 3    | 34.923                  | methyl oleate              | 40.90             |
| 4    | 35.693                  | methyl stearate            | 2.14              |
| 5    | Etc                     |                            | 1.8               |

4. Conclusion
The activated natural HCl zeolite amount of 2% (w/w) of the mass of the oil can be used for refining CPO off grade with colors to fade, removing odors, and reducing the levels of free fatty acids. The result of the synthesis of methyl ester via transesterification with the best results used a $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst with a concentration of 4% (w/w) and obtained 85.58%. The catalyst characterization of 4% (w/w) of methyl esters resulted in a density of 0.86 g/mL, a viscosity of 4.33 cSt, a refractive index of 1.45, and the acid number of 0.49 mg/g and it indicated that the methyl ester fulfilled SNI biodiesel 2015. At a concentration of 2% (w/w) yield of methyl ester, 54.90% was obtained while the concentration of 3% (w/w) produced a yield of 73.93%. The main components of the building blocks of the methyl ester transesterification of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst results with the amount of 4% were 49.64% of methyl palmitate, 5.52% of methyl linoleate, 40.90% of methyl oleate, and 2.14% of methyl stearate.
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