Conversion of rubber seed oil into biodiesel with potassium oxide alumina supported by (K₂O/Al₂O₃) catalyst

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Abstract. In this paper, we report the synthesis of K₂O/Al₂O₃ for its application as a catalyst in the transesterification reaction for biodiesel production from rubber seed oil. So far, biodiesel production has been done through transesterification of vegetable oils through homogeneous catalysts, such as NaOH and KOH. Heterogeneous catalysts are more advantageous because they are easy to separate from the products, have less corrosion, and can be reused. This study aims to investigate the effectiveness of potassium oxide alumina-supported (K₂O/Al₂O₃) solid catalysts to convert rubber seed oil into biodiesel. The K₂O/Al₂O₃ catalyst was synthesized by impregnating KOH on the support of Al₂O₃ through the inception wetness method. The catalysts were characterized by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) to detect surface structure, composition, and active phase of the catalyst. EDX analysis indicated that the catalyst consisted of 36.41% potassium, 32.89%, and 30.7% oxygen. The reaction was conducted in a two-neck glass reactor at a temperature of 65 °C, methanol to oil ratios of 10:1, during 1.5 h. The yield of biodiesel was achieved up to 96.9% at the ratio KOH: Al₂O₃ of 7.5: 2.5.

1. Introduction

Nowadays, the inadequacy of fossil fuels along with global warming due to their massive utilization leads to the consideration of alternative fuels to substitute fossil fuels [1-6]. One of the alternative fuels that are concerned to be developed and used as a substitute for fossil fuel is biodiesel. Biodiesel is one of the renewable green fuels and promising energy which has properties similar to commercial diesel. It was non-toxic, biodegradable, and produces lower emissions than petroleum diesel [7-12].

Biodiesel is generally produced via transesterification of vegetable oils and methanol using base-catalyst which is taken at moderate temperatures [13-17]. The products, glycerol and alkyl esters, are separated by settling them after the neutralization of the catalyst. Furthermore, the crude glycerol and biodiesel are purified. However, commercial biodiesel processing requires quite high production costs compared to petroleum diesel. There are two factors that affect the cost of biodiesel production (the
price of raw materials and production cost). The reduction of production costs has been tried by simplifying the process steps and minimizing waste flow. One option that has been used is transesterification with supercritical methanol (without using a catalyst) [18]. This supercritical process is very fast, it takes less than 5 minutes and does not involve a catalyst to reduce product purification costs. However, this reaction requires a very high reaction temperature, around 350-400°C and high pressure (100-250 bar) which also increases the capital cost which is quite high. [19]. The use of heterogeneous catalysts can be one of the solutions to reduce production costs because solid catalysts are easily separated from reaction products and require relatively low operating temperatures around 60-80°C. The use of solid catalysts can be more competitive with commercial diesel. Several alkaline metals such as MgO, Ca(OH)$_2$, and Ba(OH)$_2$ have been tried, all of which dissolve easily in alcohol reactants so the process is homogeneous [20-24]. Various attempts were made to obtain a better solid base-catalyst. The literature shows that there are several heterogeneous catalysts that have been reported to transform the vegetable oil into biodiesel, CaCO$_3$, Mg-Al-Olt-Bu hydrotalcite, zeolite, which are operated at relatively high pressures. Several research groups have been developed a heterogeneous catalyst, such as K$_2$O/Zeolite, CaO from eggshells, CaO from seashells and reporting that catalysts have a promising performance. Previously, the MgO catalyst supported by mesoporous silica succeeded in increasing the conversion of vegetable oil into biodiesel to 96% (reaction time 5 hours at 220°C) [25-26]. In this study, our research group successfully used the solid catalyst from the natural and synthesis material, coconut coir, palm ash (bunches), CaO, and K$_2$O from water hyrachin, which show the biodiesel yield from vegetable oils between 87.97% to 98% [27-30]. These results were obtained from several processes that are efficient and economical in the process of making methyl esters. This research explored solid catalyst potassium alumina supplying catalysts for transesterification of rubber seed oil to biodiesel. So far, the development of KOH catalyst Al$_2$O$_3$ supported is still limited in the literature. This work is concentrated on the development of alumina-supported potassium oxide (K$_2$O/Al$_2$O$_3$) catalyst for the production of biodiesel from rubber seed oil. The catalyst was prepared through a simple method of inception wetness and analyzed by SEM and EDX instrument. The effect of the KOH to Al$_2$O$_3$ ratio has been evaluated against biodiesel yield and also characterized by SNI standard.

2. Material and Methods

2.1 Materials

KOH and Al$_2$O$_3$ (as a precursor), methanol (Merck, Germany) and rubber seed oil used in the transesterification reaction into biodiesel were purchased from a market and used as received.

2.2 Catalyst preparation

KOH/Al$_2$O$_3$ catalyst at various mole ratios (1:9, 2.5:7.5, 5:0:5.0; 7.5:2.5, 9:1) was prepared by impregnation method. The process started by adding and mixing the KOH, Al$_2$O$_3$ and distilled water into the beaker glass. It was carried out using a magnetic stirrer for 6 hours. After that, the process was continued by removing the water content on the mixtures. It was dried in the oven at 120°C for 12 hours. The powder was further calcined on the furnace at a temperature of 600°C for 5 h to convert the KOH into K$_2$O. Afterward, the catalyst was stored and kept in a desiccator.

2.3 Transesterification, separation, and washing of products

The biodiesel production via transesterification reaction using rubber seed oil and methanol with K$_2$O/Al$_2$O$_3$ catalyst was carried out in the batch stirred reactor. First, the weighed catalyst (4% oil weight), methanol (1: 6 oil), and rubber seed oil were put into the reactor and operated at constant temperature (65°C) and stirred for 1.5 hours. After that, the reaction was stopped and would be continued by separating the catalyst and products with a funnel (deposited it for 48 hours). During the deposition process, two layers from the mixture would be formed. The upper layer was the methyl
ester (biodiesel), while the downside layer was glycerol. After that, the methyl ester layer was filled into the separating funnel and then continued by washing it with warm water (50°C). During that process, some esters would form an emulsion with water. It took 24 hours to get a good separation of the product (biodiesel). Afterward, a clear yellow ester layer would be formed in the upper layer. Biodiesel yield was calculated using equation 1.

\[
\% \text{ Yield} = \frac{\text{Mass of biodiesel produced}}{\text{Mass of Oil}} \times 100\%
\]

(1)

2.4 Product analysis

2.4.1. Catalyst characterization. Catalyst characterization - Scanning Electron Microscope (SEM) – Energy Dispersive X-ray Spectroscopy (EDX) was used to analyze and evaluate the morphology structure and chemical elements of the catalyst.

2.4.2. Biodiesel characterization. Biodiesel characterization consists of yield, density, viscosity, acid number, and moisture number were used to evaluate the effect of catalysts on the physical characteristics of the product (biodiesel). Density and viscosity were respectively measured using pycnometer and viscometer cannon Fenske while the acid number was using KOH base titration.

3. Results and Discussion

3.1 Characterization of K₂O/Al₂O₃ catalyst

3.1.1 SEM. The SEM patterns of K₂O/Al₂O₃ are displayed in figure 1. The selected catalyst with a magnification of 3000 times was observed.

On the SEM analysis, it can be seen that the K₂O was distributed on the Al₂O₃ perfectly. The alumina group was formed after calcining the catalyst at 600°C for 3 hours. From figure 1, it could be confirmed that the structure of catalyst (pores) was shaped like a marine coral group. It could provide better contact between catalyst and fluid in the transesterification process.

![Figure 1. SEM image of K₂O/Al₂O₃ catalyst at mole ratio 2.5:7.5.](image)
3.1.2 EDX. The transesterification reaction of RSO for biodiesel production was a surface reaction at catalytically active sites on KOH. The active sites (KOH) on the support surface (Al$_2$O$_3$) played important roles that can be evaluated by EDX. The results are presented in table 1.

From table 1, it can be seen that the catalyst consisted of 36.42% aluminum, 32.88% potassium, and 30.70% oxygen. Based on the result, the percentage of Al, K, and O$_2$ elements as well as their theoretical percentage of KOH/Al$_2$O$_3$ catalyst (impregnation process) were provided for each catalyst.

3.2 Biodiesel production using K$_2$O/Al$_2$O$_3$

3.2.1 Catalytic activity. The catalytic activity was affected by the mole ratio of catalyst (K$_2$O/Al$_2$O$_3$) and assessed based on the acquisition of fatty acid methyl ester (FAME) and saponification. The effect of various mole ratios on the catalyst performance on biodiesel acquisition is shown in figure 2.

From figure 2, it can be seen that the yield of biodiesel increased and started to decrease when the ratio of K$_2$O/Al$_2$O$_3$ was above 2.5:7.5. It was seen that the yield of biodiesel increased with the content of KOH. In this situation, the K$_2$O content was distributed well on the support surface to form K$_2$O/Al$_2$O$_3$, so it provided a better intensity to contact in the transesterification reaction process [31-32]. It could be caused by the synergy between K$_2$O and Al$_2$O$_3$ ions. A certain amount of Al$_2$O$_3$ supported could enhance the catalytic activity of K$_2$O.

| Table 1. EDX Analysis of elements. |
|------------------------------------|
| Element   | Weight % | Atomic % |
|-----------|----------|----------|
| Oxygen    | 30.70    | 46.69    |
| Aluminum  | 36.42    | 32.85    |
| Potassium | 32.88    | 20.46    |

Figure 2. Effect of various ratio of catalyst K$_2$O/Al$_2$O$_3$ on biodiesel yield.
Table 2. Catalyst analysis of K₂O/Al₂O₃ at various condition (impregnation).

| Ratio (KOH/Al₂O₃) | Density (gr/mL) | Viscosity (mm²/sec) | Acid Number (mg KOH/gr) | Moisture Content (%) |
|-------------------|----------------|--------------------|-------------------------|---------------------|
| Yield (%)         | SNI stand. >>  | 0.85 - 0.89        | 2.3 - 6.0               | Maks = 0.8          | Maks = 0.05          |
| 2.5:7.5           | 96.9           | 0.87               | 5.85                    | 0.79                | 0.05                 |
| 5:5               | 90.4           | 0.87               | 6.59                    | 0.82                | 0.06                 |
| 7.5:2.5           | 70.2           | 0.89               | 7.00                    | 0.90                | 0.06                 |
| 9:1               | 63             | 0.90               | 7.13                    | 0.96                | 0.08                 |

3.2.2 Biodiesel properties. Biodiesel product was also analyzed to identify the properties to SNI standard. Density, viscosity, acid number, and moisture content are the most important properties of biodiesel to measure the quality of the product because of their effects on the work of pressurized combustion. The values of density, viscosity, acid number and moisture content of all reactions are presented in table 2.

The combination of K₂O and Al₂O₃ as catalyst significantly affected the parameters. Based on the experiments, K₂O/Al₂O₃ catalyst with a mole ratio at 2.5:7.5 was the best combination to produce biodiesel (from rubber seed oil) that meets the SNI standard. The expulsion of other ratio combinations could be caused by the influence of tri-, di- and mono- glyceride (doesn’t react with methanol perfectly) and also by the contamination of glycerine [33].

4. Conclusion
The K₂O/Al₂O₃ catalyst was studied and applied to the transesterification of rubber seed oil into biodiesel. The best results of catalyst were obtained when the K₂O/Al₂O₃ was used at 2.5:7.5 (ratio). The analysis of the catalyst through SEM-EDX characterization found that the catalyst consisted of 36.41% alumina, 32.88% potassium, and 30.70% oxygen, with a catalyst in the form of a pore, like a sea coral structure.

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