Hydrotreating of Sunan Candlenut Oil using NiMo/γ-Al₂O₃ Catalyst for Renewable Diesel Production

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Abstract. Catalytic hydrotreating process based on NiMo/γ-Al₂O₃ has been conducted in this study using Sunan candlenut oil as the feedstock, in order to obtain renewable diesel products as well as conventional diesel. Hydrotreating process was performed with the variation of several operating conditions including pressure, temperature and weight ratio of catalyst to vegetable oils. Products obtained were then analyzed using Gas Chromatography (GC) and tested to obtain physical and chemical properties. Based on GC results, it was showed that the increase in operating pressure and temperature also increase the yield of hydrocarbon products in the range of diesel, with the highest yield of 30.95% at a pressure of 60 bar and temperature of 400 °C. The conversion and selectivity were 33.48% and 95.72%, respectively, where the reaction route tends to the decarbonylation mechanism. However, changes in the weight ratio of catalyst to the vegetable oil did not affect the overall product yield. Analysis of physical and chemical properties of the product prior to distillation showed a decrease in the value of density, viscosity, iodine numbers and acid numbers are quite significant and closer specification commercial diesel oil.

Keywords: hydrotreating, NiMo/γ-Al₂O₃, renewable diesel, Sunan candlenut oil

1. Introduction

Biodiesel is an alternative fuel that has the same properties as conventional diesel or fossil fuels. The most common type of biodiesel is FAME (Fatty Acid Methyl Ester), which is biodiesel that produced through the transesterification of vegetable oils and animal fats.

It is known that first generation of biofuels, such as FAME, faces several limitations regarding their production processes and their applications in motor vehicles. Biodiesel, in the storage process can also result in the formation of sludge after prolonged storage, and has sensitivity to hydrolysis and oxidation [1, 2]. Another important disadvantage of first generation biofuels such as FAME is that there is competition with food which is often a hot topic of discussion today. This is due to the FAME feedstock generally comes from edible oil plants such as rapeseed, soybean, coconut, palm oil and others. Therefore the use of non-edible oil is one way to reduce the dependence of the use of food oil for biodiesel raw materials. Some types of non-edible oils include, castor oil, nyamplung seed oil, Sunan candlenut oil.
candlenut oil, etc. One of the non-edible materials, namely Sunan candlenut, will be used as raw material in this study, considering the potential of this plant is quite large and its utilization is still limited.

This inefficient process is overcome by catalytic hydrotreating technology which has the ability to convert both triglycerides and free fatty acids through one reaction stage into paraffinic hydrocarbons which equivalent to conventional diesel oil [3]. The catalytic hydrotreating (HDT) process is widely used in the oil and gas refinery industry to remove undesirable elements (S, N, and metals) from the petroleum fraction, which leads to higher products (gasoline, diesel etc.) or intermediate flow (light cycle oil, gasoil etc.).

Two types of effective catalysts commonly used for the hydrotreating process are precious metal catalysts (Pd, Pt, etc.) [4] and desulfurization catalysts (Ni -Mo, Co-Mo, Ni-W, Co-W, etc.) [5, 6]. Precious metal catalysts are very effective for the hydrotreating process but the price is expensive and sensitive to the catalyst poison makes the use of this catalyst to be not feasible. Therefore selected catalysts that have been proven to be used in the oil and gas industry are desulfurization (hydrotreating) catalysts is Ni-Mo metal sulfide catalysts with alumina (γ-Al2O3) support [7-9]. NiMo / (γ-Al2O3) is one of the most commonly used catalysts in the hydrotreating process for the middle and heavy distillate products in petroleum refiners. This catalyst has a high hydrogenation activity and adequate acidity (mild acidity) which is very suitable for the conversion process of triglycerides into renewable diesel products [6].

Therefore, in this research, hydrotreating of Sunan candlenut oil will be conducted using a NiMo / (γ-Al2O3) Al2O catalyst that has been characterized. Hydrotreating process will be carried out with moderate temperature conditions between 300-400°C and under high hydrogen pressure which is between 30-60 bar and using a sulfated bimetal catalyst in the form of NiMo / (γ-Al2O3). The choice of catalyst is based on the target product to be obtained in the form of straight chain hydrocarbons as the main product in the diesel fuel fraction range. The catalyst was prepared with a certain metal composition according to the literature where Ni metal as a promoter and Mo metal as a precursor. Then the hydrotreating operating conditions using NiMo / (γ-Al2O3) catalyst will be optimized in an autoclave reactor which runs with a semi-batch operation. Optimization is carried out by adjusting the ratio of the weight of the catalyst to the kemiri sunan oil feed, the flow rate of hydrogen gas entering the reactor to achieve optimal conditions of reactor pressure and the best operating temperature that results in high conversion and selectivity, to obtain high yield of renewable diesel products.

2. Materials and Method

2.1. Materials

The materials used in this study were: NiMo/γ-Al2O3 catalyst that has been previously prepared, Sunan candlenut oil, hydrogen gas and nitrogen gas.

2.2. Degumming of vegetable oil

Degumming was done to remove contaminants in the vegetable oil. A 3 L of Sunan candlenut oil was heated to a temperature of 90°C and then added with H3PO4 and let the reaction performed for 10 minutes. The temperature was raised to 110°C, and then bentonite was added and stirred for 30 minutes. Afterwards, the mixture was filtered to separate the bentonite that has bonded the gum from the oil.

2.3. Hydrotreating

Hydrotreating using NiMo/γ-Al2O3 catalyst was carried out in an autoclave reactor by preparing the feed to be reacted first. Sunan candlenut oil as much as 500 mL was placed in a 1 L capacity reactor equipped with a stirrer, an electric heating element and exhaust gas path that comes out from the reactor. The entire operation of the reactor was computerized and automatically controlled. Sunan candlenut oil was inserted into the reactor with N2 gas injected with a reactor pressure of 30 bar. Afterwards, the gas phase chamber in the reactor was flushed by injecting and removing nitrogen gas in a row for 3 times and then replace it with hydrogen gas in the same way 3 times. After the operating conditions were reached, for
example 375°C in temperature and 40-42 bar in pressure or 385°C in temperature and 60-62 bar in pressure, the reaction was performed for 1-2 hours. After reaction, the solid was removed and placed in a ceramic container and then dried in the oven for 1 hour at 100°C. The liquid product, which was separated from the catalyst, was a renewable diesel product that should be filtered twice for the remaining dissolved catalyst to be separated from the renewable diesel product.

3. Results and Discussions

In the synthesis of renewable diesel through the hydrotreating process, operating conditions greatly affect the composition of the resulting product. This is because operating conditions will determine the direction of the reaction and the resulting product. In this study, as a first step, the hydrotreating operation of Sunan candlenut oil was carried out under pressure conditions of 30 bar and 375°C with the amount of catalyst used as much as 5 g (1% by weight of the volume of oil (w/v)). Furthermore, under conditions of constant temperature and weight of the catalyst, the operating pressure varies to 40, 50 and 60 bar.

3.1. Effects of pressure on the composition of renewable diesel products

In a hydrotreating reaction, operating pressure affects the composition of the resulting product. The composition of renewable diesel products is quantitatively shown in Figure 1. Based on the results obtained, it can be seen that the resulting product already contains hydrocarbon compounds in the diesel oil range. But in terms of quantity, the acquisition of diesel products is still relatively small, amounting to 17.61%.

Based on the results of the analysis, the products produced from the hydrotreating process of Sunan candlenut oil using a NiMo/Y-Al2O3 catalyst can be described in Figure 1. Based on this figure, it can be seen that the trend in the acquisition of each product has changed with increasing operating pressure.

Figure 1. Effect of pressure on the composition of renewable diesel products

Based on Figure 1, it can be seen that increasing the operating pressure will increase the intermediate product yield in the range of <C18 (intermediate distillate) and decrease the amount of C19-C25 heavy fraction product. Meanwhile, the light fraction product in the form of gas did not experience an increase (stagnant). This indicates that the increase in operating pressure can increase the conversion and selectivity of product fractions, especially hydrocarbon products in the diesel range.

3.2. Effect of temperature on the composition of renewable diesel products

The operating temperature also affects the hydrotreating process and the resulting product. The effect of operating temperature on product composition under a constant pressure condition of 60 bar can be
observed in Figure 2 below. The best results were obtained at an operating temperature of 400°C with maximum yield for diesel hydrocarbon range of 30.95%.

![Figure 2. Effect of temperature on the composition of renewable diesel products](image)

The effect of changes in operating temperature on the composition of the resulting renewable diesel products can be observed in the graph in Figure 2. Based on the results, almost all hydrocarbon fractions of renewable diesel products increase with increasing operating temperatures. However, a very significant increase occurred only in the fraction of C14-C18 diesel products. This is inseparable from the role of the catalyst which is designed to have a certain acidity to direct the product to the diesel hydrocarbon range. The lighter fraction of diesel also experiences an increase due to an increase in temperature triggering cracking of some diesel products into smaller hydrocarbon molecules or short chains. Whereas heavy oil hydrocarbon products have decreased because some of the triglycerides detected by GC as heavy oil have been converted more in line with the increase in operating temperature. The temperature in the biodiesel synthesis is an important view that need to be monitored [10, 11].

3.3. The effect of catalyst weight on the composition of renewable diesel products

The condition that was also varied in this study was the weight of catalyst used in the hydrotreating process. The catalyst weight variation test was carried out to see the effect of catalyst weight on product acquisition. The catalyst weight variation was carried out under 2 operating conditions to compare the performance of the catalyst under different operating conditions, such as the catalyst weight of 10 and 15 g under 60 bar pressure and 400°C temperature and the catalyst weight of 15 and 20 g at 60 bar pressure and 385°C temperature as in Figures 3 and 4.

Based on the results obtained, the weight of the catalyst does not affect the composition of the product in the hydrotreating process. This is due to the variation of catalyst weight does not significantly affect its activity as does the addition of the amount of active metal composition or changes in the shape of the catalyst. This can be seen at a temperature of 400°C, the composition of <C18 and C19-C25 components is not much different both in the weight of catalyst 10 and 15 g as well as the weight of 15 and 20 g at 385°C. Thus, it can be seen that the variation of catalyst weight in the hydrotreating process of Sunan candlenut oil does not affect the acquisition and composition of hydrocarbon products.
Figure 3. Effect of catalyst weight on product composition at P: 60 bar and T: 400°C

Figure 4. Effect of catalyst weight on product composition at P: 60 bar and T: 385°C

3.4. Chemical physical properties test

The products obtained from hydrotreating of Sunan candlenut oil using NiMo/γ-Al₂O₃ catalyst were tested by physical and chemical properties to see the suitability of its quality to commercial diesel oil. These results can be seen in Table 1. In the table, the product showed that the results of hydrotreating Sunan candlenut oil have similar properties with pertadex and also seen significant changes when compared with the characteristics of Sunan candlenut oil feed.

The physical properties of the product in the form of density have met the specifications, but the viscosity is still quite high above the maximum limit of pertadex. This is because there are still compounds that contain double bonds in the form of olefins. When viewed from the properties of the iod number, it can also be seen that there are still many unsaturated compounds contained in the liquid hydrocarbon products produced by hydrotreating Sunan candlenut oil. The results of the acid number analysis show the acidity level of the product is very small or even undetectable. This indicates that the product does not already contain carboxylic acid compounds as an agent contributing acid numbers and
is also a compound between the results of the termination of glycerol backbone groups that form carboxylic acids and propane gas.

**Table 1. Chemical physical properties of hydrotreating Sunan candlenut oil**

| Characteristics            | Candlenut Sunan | Product 351* | Product 352** | Pertadex 
|----------------------------|-----------------|---------------|----------------|---------- |
| Density 15°C (kg/m³)       | 0.92            | 0.848         | 0.865          | 0.82-0.85 |
| Viscosity 40°C (mm²/s)     | 82.74           | 38.99         | 30.06          | 3.5      |
| Acid value (mgKOH/g)       | 28.91           | -             | -              | -        |
| Iodin number               | 129.54          | 61.44         | 64.28          | -        |

* P: 60 bar, T: 385°C, catalyst weight: 15 g
** P: 60 bar, T: 385°C, catalyst weight: 20 g

Based on the results, when compared with the initial conditions of oil, the physical and chemical properties of products obtained showed a significant change in the properties of almost all of the analyzed characteristics, such as viscosity, acid number and iodine number. This change occurs due to the triglyceride compound in the feed of Sunan candlenut oil has been converted and undergoes a series of routes or reaction mechanisms that occur to produce diesel oil in the form of straight chain paraffinic hydrocarbons as described in the discussion related to the previous reaction mechanism.

3.5. *Calculation of conversion and selectivity*

Calculation of conversion and selectivity in this study takes a reference or basis from the amount of triglyceride feed before and after the hydrotreating reaction operation.

**Figure 5.** Conversion profile of the product: (a) before distillation and (b) after distillation

Figures 5 (a) and 5 (b) showed the concentration profile of each product obtained from the hydrotreating of Sunan candlenut oil under various operating conditions, both before and after distillation. Before distillation, it is known that product samples 340 (P: 60 bar, T: 400°C) and 349 are ranked as the first and second largest conversions, specifically more than 50%. Meanwhile, among the products that have been distilled, it is known that product samples 336 (P: 60 bar; T: 400°C, catalyst weight: 10 g) and 346 (P: 60 bar; T: 400°C, catalyst weight: 15 g) are the products with the first and second largest conversion values, specifically above 30%.

The acquisition value of the conversion between products before and after the different distillations is due to the calculation of products after distillation based on the range of boiling point range of 300-
350°C only, while there are still other products in the lower boiling point range of 100-200°C and 200-300°C.

The measurement of the performance of Sunan candlenut oil hydrotreating operations, apart from being calculated by conversion parameters, can also be done with the selectivity parameters in order to see the yield of the product desired compared with the product as a whole. The selectivity value of the product can be grouped according to variations in operating conditions both variations in pressure and temperature in order to obtain the best operating conditions that provide the highest selectivity value. The selectivity profile of variations in pressure and temperature can be seen in Figures 6 (a) and Figure 6 (b) where an increase in operating pressure and temperature will increase the desired product selectivity.

4. Conclusion
The hydrotreating results on variations in operating conditions show the presence of straight chain paraffinic hydrocarbon compounds even though the yields are not optimal. The increase of operating pressure is able to increase the conversion and selectivity of middle distillate product fraction, especially hydrocarbon products in the diesel range, which is 17.61%. Likewise, the variation in operating temperature gives a worth result, where almost all hydrocarbon fractions of the product increase with the increase in operating temperature, but the highest yield is in the diesel fraction of 30.95%. From the catalyst weight, it can be seen that the variation of catalyst weight does not significantly influence the product acquisition.

5. References
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