

Catalytic hydrogenation of straight vegetable oil using NiMo/Al₂O₃ catalyst for biodiesel production

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Abstract. The attractiveness of biodiesel as an alternative fuel compared to fossil fuels because it has many advantages such as the availability of abundant raw materials, more environmentally friendly, high combustion efficiency, low sulphur content, high cetane number and biodegradability. Making biodiesel from straight vegetable oil (VGO) has been done through the catalytic hydrogenation process. A VGO of calophyllum inophyllum oil was treated via degumming and neutralisation to remove all impurities before hydroprocessing. Hydroprocessing was carried out in a 500ml autoclave at 30 – 50 MPa of initial hydrogen pressure, 300 – 400°C of reaction temperature and equipped with stirrer and cooling system. NiMo/Al₂O₃ catalyst was activated with CS₂ mixture at 370°C prior to the reaction. Some physical and chemical properties of the catalytic hydroprocessing product have been investigated in accordance to ASTM standard. The measurement result of product varies according to the operation condition. The result showed that calophyllum inophyllum oil can be used as raw material for biodiesel production over NiMo/Al₂O₃. Sulfided NiMo/Al₂O₃ catalysts are preferred due to high diesel yield.

1 INTRODUCTION

Indonesia's energy needs continue to increase along with increasing human needs as a result of modernization and industrialization. The fossil energy resources of its availability are increasingly limited and non-renewable. The burning of fossil energy can cause environmental pollution to degrade air quality, besides the carbon monoxide (CO), sulfur oxide (SO_x) and nitrogen oxide (NO_x) exhaust gases from combustion also cause global warming. So that, it is very important to develop alternative fuels that are more environmentally friendly and abundant availability. Biodiesel is one of the most promising forms of future energy for diesel engines. This is because of the availability in large volumes, biodegradable, non-toxic, and environmentally friendly [1,2]. The Government of Indonesia has issued a policy in the field of energy that is increasing the role of new and renewable energy in the national energy mix through Presidential Regulation No. 5 of 2006 on National Energy Policy. And as implementation of the policy has also been issued Regulation of Minister of Energy and Mineral Resources No. 25 of 2013 for the acceleration and improvement of mandatory use of biofuels [3]. Biodiesel in diesel oil for transportation is increasing from 10% in 2013 to 25% by 2025. This mandatory policy of biofuel is one of the prominent policies set by the government in order to encourage the use of biofuel, especially biodiesel, reducing dependence on diesel oil imports, foreign exchange, and supporting macroeconomics.

Indonesia is rich in renewable energy resources especially for biodiesel production. Biodiesel can be made from various kinds of raw materials, such as palm oil, jatropha, algae, canola as well as various biomass [4,5,6,7]. Each biodiesel product has its own characteristics in accordance with the raw materials and processes used [8]. Some researchers [9-12] find a fact that there are many similar physical and chemical properties between biodiesel and diesel oil, and even biodiesel is said to have several advantages over diesel oil such as having a higher cetane number, almost no sulphur, no aromatics and contains 10-11% by weight of oxygen. This characteristic of biodiesel that greatly helps in lowering emissions of hydrocarbons, carbon monoxides and particulates [13-15]. However, on the other hand there are some disadvantages of biodiesel that inhibit its use of kinematic viscosity and higher density, and have lower calorific value than diesel oil.

That is why many scientists conduct research and investigation of mixing biodiesel with diesel oil in various mixing variations to investigate suitability as fuel for existing diesel engines. And the results show that the problems associated with biodiesel can be overcome by using a mixture of biodiesel-diesel. They also found a better heat efficiency phenomenon as well as reduced emissions of HC, CO and NO_x and particulates [16,17]. Some researchers [18-23] also suggest the mixing in which B20 (20% biodiesel in diesel-biodiesel blends) can provide better performance compared to using its own diesel fuel. They found that B20 has improved

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density, viscosity and flash points and near calorific value with diesel that results in better performance. In addition, many efforts were made to improve the quality of diesel oil from a variety of raw materials has been reported by some researchers so that biodiesel can be used directly as fuel replacement fuel without having to be mixed with diesel. Most researchers refer to the petroleum purification process whose technology has proven and used in many oil refineries worldwide. Generally the researchers used NiMo / Al₂O₃, CoMo / Al₂O₃ catalysts. [24-26].

This research aims to produce biodiesel oil from a straight vegetable oil (VGO) such as callophyllum inophyllum oil with catalytic hydrogenation process using NiMo / Al₂O₃ catalyst. To further accelerate the process of hydrogenation, the content of gum in the callophyllum inophyllum oil was removed first by degumming and neutralization process. The operating conditions in the biodiesel production was greatly affect the amount of biodiesel product. This study will provide a significant contribution in addressing the energy crisis that is still leaning on fossil energy as well as obtaining an alternative energy source that can be used directly as a substitute for fuel oil without having to change the existing infrastructure.

2. Research Methods

2.1. Raw Materials

Callophyllum inophyllum oil used in this study was obtained from Cilacap region of Central Java which is famous as callophyllum inophyllum planting center. The crude of callophyllum inophyllum oil was pretreated by degumming and neutralization. In the degumming process, distilled water was used to remove gums and other impurities. Oil and distilled water were heated at 80°C and stirred strongly for 25 minutes. Triglycerides and water were separated using a separation funnel. NaOH was used in the process of neutralization.

2.2. Catalyst

The catalysts used in this study were commercial catalysts such as NiMo/Al₂O₃ and NiW/Al₂O₃. NiMo/Al₂O₃ contained NiO 4.0 - 6.0wt%, and MoO₃ 20.0 - 24.0wt%, and Al₂O₃ 70-76wt%. While NiW/Al₂O₃ contained NiO 5.0wt%, WO₃ 22wt% and Al₂O₃ 73wt%. NiMo/Al₂O₃ and NiW/Al₂O₃ catalysts were converted to NiMoS and NiWS via sulfidation process using CS₂ at 370 ° C for 4 hours prior to use.

2.3. Catalytic hydrogenation procedure

The catalytic hydrogenation reactions were carried out in an autoclave batch reactor of 500ml equipped with a stirrer and cooling system as shown in Fig. 1. 170 g of VGO and 5wt% of NiMo/Al₂O₃ or NiW/Al₂O₃ were loaded in the autoclave. The oxygen content in the autoclave reactor was discharged through purging with hydrogen gas. A leak test was then performed for 2 hours to ensure no leakage occurs during the reaction. The initial reaction pressure (H₂) were 30 and 50 bar, with a reaction time of 1 hour at a predetermined

temperature. After completion of the reaction, the oil product was separated from the catalyst by filtration.

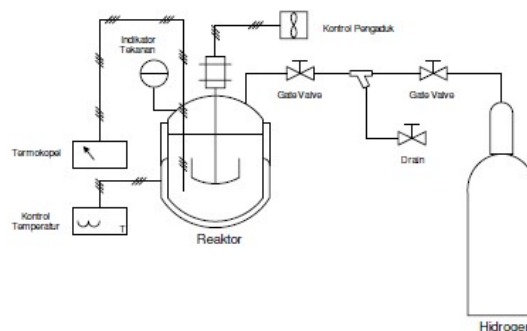


Fig 1. The batch reactor system for the hydrodeoxygenation process

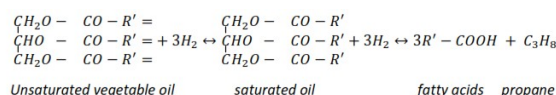
2.4. Product Analysis

The gas product was analyzed using GC Shimadzu 2004 both TCD and FID detectors. GC TCD used the porapak Q column, while GC FID used the 5A molecular sieve column. GC TCD was used for analyzing CO, CO₂ gas, while GC FID was used for analyzing propane and other organic gases. Liquid oil products were analyzed using GC FID from Bruker, while the calorific value was measured by IKA C6000 from Global Calorimeter based on ASTM D-240.

3. Results and Discussions

VGO (callophyllum inophyllum oil) have high free fatty acid content (FFA) between 17,6% and 22,3%. Crude oil may have different FFA values depending on several factors such as long harvest, incomplete drying, and hydrolysis during storage. To meet the biofuel specifications, this crude oil content of FFA should be less than 1%. FFA and metals contained in the raw material of the oil should be removed as it can precipitate into coke and cause deactivation of the catalyst.

Many reactions may occur during the hydrogenation process of vegetable oils. The reaction starts with hydrogenation to form saturated triglycerides. By adding excess hydrogen, then form three fatty acids (also called carboxylic acids) and propane. The reaction as bellow;



The next stage is hydrogenation to saturate fatty acids. Fatty acids can react to many products through decarboxylation, decarbonylation, and deoxygenation. In this reaction, oxygen removal may occur. Where R is a fatty acid structure such as oleic (C18:1), linoleic (C18:2) and palmitate (C16:1). Therefore, the final diesel product in the range of C15-18 refers to the fatty acid composition in the raw material.

Deoxygenation, an exothermic reaction, can eliminate oxygen by producing water, n-alkanes have the same amount of carbon as fatty acids. Decarbonylation and decarboxylation remove oxygen in the form of CO, CO₂ and water. N-alkanes have lost one carbon compared to the initial fatty acids. For certain fatty acids may form alcohols, esters and other compounds through cyclization, formation of alcohols and esters.

It can be seen that decarboxylation, decarbonylation and reduction are the main reactions in paraffin formation, with by products being CO₂ and CO. The formation of n-paraffins via decarbonylation would be preferred because it does not require H₂. Table 1 and Table 2 show the effect of operating conditions with NiMo/Al₂O₃ and NiW/Al₂O₃ catalysts.

Most products are solid at room temperature. This indicates that the product still contains hydrogenated oils (saturated vegetable oils) and stearic acid as a product between [25,26]. The wax-wax phase is formed due to long chains and paraffin branches with high melting point.

Table 1. Effect of operating conditions using NiMo/Al₂O₃ catalyst

Parameter	Catalyst (%)	Initial Pressure (bar)	Reaction Pressure (bar)	Temperature (oC)	Form	Calorific value (J/g)	Liquid product (%)	Diesel Yield (%)
Temperature	5	30	50	300	Liquid	39.100	84,45	0,32
	3	30	70	350	Solid	39.406	84,41	5,87
	3	30	70	400	Solid	39.539	89,83	8,85
Pressure	5	30	70	350	Solid	39.117	81,06	1,2
	3	50	80	330	½ solid	39.101	80,88	1,6

Table 2. Influence of operation condition using NiW/Al₂O₃ catalyst

Parameter	Catalyst (%)	Initial Pressure (bar)	Reaction Pressure (bar)	Temperature (oC)	Form	Calorific Value (J/g)	Liquid Product (%)	Diesel Yield (%)
Temperature	3	30	50	300	Liquid	38.920	86,73	0,61
	3	30	70	350	½ Solid	39.279	90,82	1,31
	3	30	70	400	Solid	40.475	80,71	8,39
Tekanan	3	30	65	350	½ Solid	39.279	91,67	1,31
	3	50	80	350	Solid	39.372	86,78	1,58

It can be derived by fractionation/distillation, mixing with additives and de-waxing or isomerization [28,44]. Catalytic de-waxing can reduce the pour point by isomerization and/or hydrocracking to shorten the length of the chain. Calorific value was also analyzed to see the amount of energy or heat released during combustion. However, the calorific value results are not significantly high. Crude oil from calophyllum inophyllum has a calorific value of 38,811 J/g, which means it does not differ significantly. The calorific value for a liquid product tends to increase at higher temperatures. Liquid product at 400oC with NiW/ Al₂O₃ catalyst has the highest heat value of 40,475 J/g. Figure 2 displays the effect of the operating temperature on the diesel product.

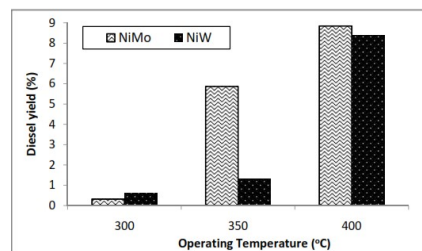


Fig. 2 Effect of temperature operation on diesel products

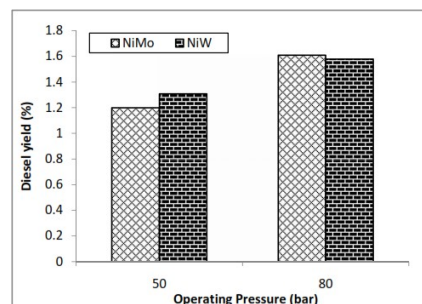


Fig. 3 Effect of pressure operation on diesel products

Temperature has an important role in this process, it can be seen that the pressure has a less conspicuous impact on the calorific value and yield of the product. Figure 3 shows the effect of the operating pressure on the diesel product. Diesel products increase slightly as pressure increases. This low pressure diesel at low pressure relates to a low hydrogen partial pressure which can decrease the mass transfer limit on the surface of the catalyst [25]. These results are similar to those reported by Srifa et. al. (2014). Hydrogen pressure has no significant effect on increasing the yield of diesel. The disadvantage of using calophyllum inophyllum oil as raw material is that unsaturated fatty acids (oleic acid and linoleic acid) are present in the triglyceride branch which means consuming more hydrogen than palm oil. Palm oil contains most of the palmitic acids that have saturated fatty acids making it easier to process and consume less hydrogen [29].

The ratio of H₂/oil, has a significant difference in product yield. Figure 4 shows the effect of the H/Oil ratio on the diesel product. The higher the ratio of H₂/oil, the higher the product. The duration of the reaction is also a parameter seen in this study. Table 3 shows that by extending the reaction time of diesel products increases from 0.32% to 0.76%.

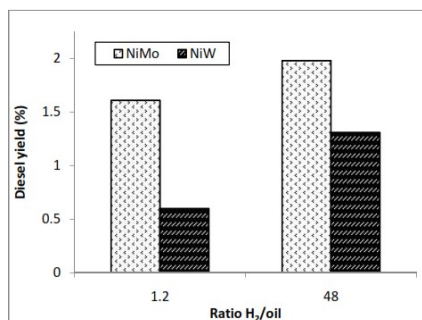


Fig 4. Effect of H / oil ratio on diesel product

Table 3. Effect of reaction time using NiMo / Al₂O₃ catalyst

Time (hour)	Catalyst (wt%)	Initial pressure (bar)	Reaction Pressure (bar)	Temperatur (oC)	Form	Liquid Product %	Caloific Valueae (J/g)	Yield Diesel (%)
3	5	30	50	300	Liquid	84,45	39100	0,32
6	5	30	50	300	Solid	82,55	39207	0,76

Based on these results, NiMo tends to produce diesel products that are higher than NiW. Although NiW has a stronger hydrogenation capability than NiMo, high selectivity to diesel is obtained using NiMo/Al₂O₃ catalysts compared with NiW/Al₂O₃ [28]. Sodas with moderate acidity are indispensable as buffers with high acidity can lead to cracking which results in lighter alkanes and reduced selectivity toward diesel products [31]. The catalyst activity used was not so good, it can be seen from the very low diesel product. It can be assumed that the surface contact between the reactants and the catalyst was so low that the diesel product was also low. In addition, large triglyceride molecules hardly diffuse into the catalyst [28]. Another reason is the high oxygen content and low sulfur content of vegetable oils of about 30% by weight and 3 wt% leading to the oxidation of the catalyst and subsequently causing deactivation of the sulfide catalyst [32].

4 Conclusion

- Callophyllum inophyllum oil was treated with degumming, neutralization, and drying process to remove all dirt (gum, FFA, and metal).
- Callophyllum inophyllum oil can be used as raw material for biodiesel production using NiMo/Al₂O₃ and NiW/ Al₂O₃ catalysts. The result of bio-iesel oil with NiMo / Al₂O₃ catalyst is higher than using NiW/Al₂O₃ catalyst.

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