Transesterification of jatropha curcas oil for biodiesel production Over NiO catalyst

Y W Mirzayanti¹, N P Asri², L Marlinda³, M A I Muttaqii⁴

¹Department of Chemical Engineering, Faculty of Industrial Technology, Institute Technology of Adhi Tama Surabaya, Jl. Arief Rahman Hakim No. 100 Surabaya, Indonesia.
²Department of Chemical Engineering, Faculty of Industrial Technology, University of WR. Supratman, Jl. Arief Rahman Hakim No.14, Surabaya, Indonesia.
³Department of Chemistry, Faculty of Science and Technology, University of Jambi, Jl. Raya Jambi-Muara Bulian KM 15 Mendalo Indah Muara Jambi-Jambi, Indonesia.
⁴Research Unit for Mineral Technology, Indonesian Institute of Sciences, Jl. Ir. Sutami Km. 15, Tanjung bintang, South Lampung, Indonesia, 35361.

*corresponding author: yustiawulandari_che@itats.ac.id

Abstract. The research paper deals with Jatropha curcas oil's transesterification process using the NiO catalyst as a heterogeneous catalyst to produce Biodiesel. The batch reactor in this process. Excess methanol is needed to shift the equilibrium towards the product and enlarge Biodiesel. The research study about the effect mole ratio of methanol: Jatropha curcas oil. The ratios are 12:1, 15:1, 18:1, and temperature of the reaction of 60, 65, 70°C. Experiment verification of the predicted yield and characterization of Biodiesel produced. The analysis biodiesel product by Chemical characterization using Gas Chromatography (G-C) analysis and ASTM 6751 standard used for the physicochemical properties. The maximum process conditions for the biodiesel yield by transesterification of Jatropha curcas oil over NiO catalyst 59.8% and the mole ratio of 15:1 methanol: Jatropha curcas oil. The 65°C reaction temperature used in this process enhances the transesterification reaction by observing 5 hours with a high yield of Biodiesel.

1. Introduction

Biodiesel is a fuel that is processed from the esterification of fatty acids free or naturally available triglyceride transesterification is contained in renewable natural resources such as plant oils and fats. Biodiesel has attracted many researchers to study its synthesis with a wide variety of feedstock sources. Several types of oil that work converted into biodiesel, including soybean seeds, rapeseed, sunflower seeds, oil palm, nuts, camellina, canola, cotton, pumpkin, castor seeds, and fat [1]. Search for petroleum-based renewable fuel alternatives in concern with sustainable energy and clean environment develops different alternative technologies like fuel cell, electric power, hydrogen, and biomass-based fuels. Focus on renewable Fuel begins with the direct use of vegetable oils as an alternative to petroleum diesel in the diesel engine. Using vegetable oil as a fuel for diesel engines is an existing technique from the engine development era [1]. Generally, plant oil or animal fat is an ester of saturated and unsaturated monocarboxylic acids with trihydric alcohol glycerides. These esters
are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as transesterification.

In general, catalysts can be divided into two types, namely homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts are catalysts that have the same phase as the reactants, including transition metal compounds and acid-base catalysts. Homogeneous catalysts generally react with one or more reactants to form a chemical intermediate which then reacts to form the final product of the reaction, in a process that restores the catalyst [2][3]. The weakness of this homogeneous catalyst is the difficulty of separating from the product so that the equipment needed for the separation process is more and more costly production will be higher. The process carried out with this catalyst is not environmentally friendly because of the large amount of waste from the separation process and is corrosive. Soap formation through a saponification reaction occurs with a primary homogeneous catalyst. Heterogeneous catalysts are a more profitable alternative for methanol ester synthesis reactions because heterogeneous catalysts are in phase with the reactants and product compounds so that they are easy separated from products, can be reused, and non-toxic and environmentally friendly [4].

This study aimed to develop biodiesel production process. *Jatropha curcas* oil was used through a transesterification process using a NiO catalyst as a heterogeneous catalyst, which was carried out in a batch reactor. The molar ratio between methanol - *Jatropha curcas* oil, reaction time, reaction temperature, fatty acid content, and water in the oil are factors that influence the transesterification reaction. In the transesterification process, methanol is more widely used because it is cheaper than other alcohols. Excess methanol is needed to shift the equilibrium towards the product, and enlarge biodiesel.

2. **Experimental methods**

The feedstock oil used in this experiment was extracted from *Jatropha curcas* oil. *Jatropha curcas* oil content unsaturated hydroxyl fatty acid, cis 9,12 hydroxy octadecanoic acid, which is commonly called risonoleic (ricinoleic acid), 89.5%. Methanol 99.8%, n-Hexane 98% from Merck, and KOH were bought from Sigma Aldrich and of analytical grade. This experiment used mole ratio methanol:*Jatropha curcas* oil 12:1, 15:1, 18:1. Variation of the temperature of reaction used 60, 65, 70°C.

During the experiment, put methanol with a concentration mole ratio of 12:1 to *Jatropha curcas* oil into a three-neck flask, then add the 3% NiO catalyst between methanol with *Jatropha curcas* oil and stir until homogeneous. Next, add the *Jatropha curcas* oil slowly in a three-neck flask, which already contains methanol and catalyst. Then, refluxed for 5 hours at 60°C accompanied by stirring and cooling. The reflux product is filtered, and the filtrate is put into a separating funnel and allowed to stand for 30 minutes until 2 phases are formed. The methyl ester phase is washed with warm distilled water where the temperature is around 50°C until the washing solution is neutral, then let it stand then poured so that the glycerol separated with the methyl ester phase. The same treatment for variations in the mole ratio of methanol and castor oil 15:1, and 18:1, and temperature of the reaction. Pure methyl esters are analyzed for their characteristics. Chemical characterization using Gas Chromatography (GC). The physicochemical properties of the Biodiesel were characterized according to ASTM 6751 standard.

3. **Results and Discussion**

This research was conducted in several steps, i.e., the transesterification process and product analysis. The catalyst used a 3% NiO catalyst between methanol with *Jatropha curcas* oil NiO. The methyl ester is produced from the reaction of *Jatropha curcas* oil with methanol, which calculates concentration using Gas Chromatography (GC) so that the desired yield can be obtained. The result of the reaction of making methyl ester forms three separate phases, where the top layer is the remaining unreacted methanol, the middle layer is methyl ester, and the bottom layer is the catalyst, as shown in
Figure 1. The methyl ester obtained from the transesterification reaction separated from the catalyst and the remaining reactants, then the methyl ester is GC tested and its characteristics.

3.1. The Effect of Comparison of Jatropha curcas Oil Moles ratio with Methanol on Heterogeneous Transesterification Process on Methyl Ester Yield based on Reaction Temperature.

Based on the effect of variations in the methanol : Jatropha curcas oil mole ratio in the heterogeneous transesterification process, the highest yield was 59.80%. Based on these results, it explains that the mole ratio of methanol to Jatropha curcas oil has a large effect on the formation of methyl ester yield by taking the basis of the number of moles of castor oil is 1 mol, so the following Figure 2 is obtained:

Figure 2. The relationship between methanol-Jatropha curcas oil molar ratio based on variations in reaction temperature

In this study, the use of 12:1 mole between methanol and castor oil resulted in a yield of 0.07%, incomplete conversion of methyl ester was due to inadequate methanol concentration to shift the equilibrium reaction towards the formation of methyl ester products. The most significant yield is obtained using a 15:1 mole ratio of methanol to castor oil, which is 59.80%. The ratio of alcohol to
fatty acids is 15:1, according to previous the report, which states that this ratio is the optimum molar ratio of methyl ester synthesis with heterogeneous acid catalysts [5]. From this result, it can be predicted that the magnitude of the mole ratio used in the heterogeneous transesterification reaction is caused by the collision. The collision of methanol against NiO is used and reacts with the triglycerides in the sample so that it requires a lot of methanol to react optimally. Meanwhile, the use of an 18:1 mole ratio between methanol and castor oil resulted in a yield of 9.077%, the conversion of methyl ester was not maximum and decreased due to the use of a large enough mole ratio so that the catalyst content decreased in line with the increase in methanol content. Besides that, alcohol is a particle that is sensitive to water [6]. In a previous study by [8] Kim et al. (2013) regarding the hydrotreatment of soybean oil to produce renewable diesel fuel using a Ni catalyst, it shows that the Ni catalyst can produce liquid products \( n-C_{17}/(n-C_{17} + n-C_{18}) = 0.93-0.96 \), which indicates that most of the triglycerides are deoxygenated by decarboxylation and/or decarbonylation. When Ni catalyst is used, both the conversion value and the diesel yield increase with the increase in reaction temperature with a maximum temperature of 400°C, mainly due to endothermic decarboxylation and decarbonylation reactions [9]. The high decarboxylation and decarbonylation values in using a Ni catalyst indicate that the C – C bond is cut. Catalysts containing transition metals as active materials such as Ni, Pd, and Pt show catalytic activity on cutting C – C bonds [9].

Meanwhile, the presence of water and free fatty acids inhibits the transesterification reaction, which will decrease the conversion of the methyl ester product. The maximum mole ratio obtained through this study is 15:1 with a conversion result of 59.80%. The yield of 59.80% is far from what we expected, previous research by [8] used a nickel catalyst for transesterification of soybean oil with a maximum methyl ester conversion of 87% at 65°C. The magnitude of the effect of the reaction temperature on the heterogeneous transesterification process, according to the yield is 59.80%. From this percentage, it can be explained that temperature has an influence on the formation of methyl ester yield. At 60°C, the resulting yield is low, namely 0.3655%. This is because methanol does not mix homogeneously with Jatropha curcas oil because, at this temperature, it is less than the boiling point of methanol so that the reaction does not run correctly. In this study, the most significant yield was obtained using a temperature 65°C reaction, which is 59.80%. At this temperature, it is a very suitable temperature for the reagents to mix homogeneously because methanol boils at 65°C. There is a deviation for the transesterification reaction at 70°C, obtained a methyl ester conversion of 22.91%. In this case, the temperature is too large, so that the methanol used evaporates.

3.2. The physicochemical properties of the Biodiesel at 65°C

The comparison of density with Molar Methanol – Jatropha curcas oil (12:1, 15:1, 18:1) at 65°C for 5 hours. The quality standard of methyl ester according to SNI 04-7182-2006 stipulates that the density of methyl ester at 40°C is in the range 0.85 – 0.89 g.cm\(^{-3}\). The methyl ester density produced by heterogeneous transesterification in this experiment has an average value of 0.8828 g.cm\(^{-3}\). The density of Biodiesel obtained through heterogeneous transesterification has a value of 0.8828 g.cm\(^{-3}\) and has a viscosity of 6.431 mm\(^2\).s\(^{-1}\) (cSt) according to the comparison standard. Meanwhile, the acid number is 0.563 mgKOH.g\(^{-1}\), so it can be concluded that the quality of the Biodiesel obtained meets the standard limit. The quality standard of methyl ester, according to SNI 04-7182-2006 stipulates that the density of methyl ester at 40°C ranges from 0.85 to 0.89 g.cm\(^{-3}\).

In addition to other physical properties, namely viscosity. It can be explained that the optimum viscosity conditions in this experiment are using a 15:1 mole ratio with a value of 15.45 cSt. The lower the mole ratio of methanol : Jatropha curcas oil, the greater the resulting viscosity as in the mole ratio of 12:1 with a viscosity of 23.03 cSt, but the lower viscosity is also produced at a mole ratio of 1:18 of 19.87 due to the resulting yield. The comparison is also of little value. Kinematic viscosity is one of the main parameters in determining the quality of methyl ester because it has a major influence on the effectiveness of methyl ester as a fuel. Vegetable oil has a viscosity far above the viscosity of diesel fuel. This is an obstacle to the direct use of vegetable oil as fuel. The kinematic viscosity of the methyl ester produced in this experiment averaged 6.437 cSt, which is much higher than the quality standard.
of methyl ester, according to SNI 14-7182-2006 which only ranged from 2.3 to 6.0 cSt at Table 1. The free fatty acid is a measure used to determine the properties of the resulting methyl ester, which is the higher the free fatty acid content, the resulting in the formation of ash during biodiesel combustion. The free fatty acid produced in this study is 0.563 mgKOH.g⁻¹, and does not exceed the quality standard of SNI 14-7182-2006 methyl ester, which has a maximum limit of 0.8 mgKOH.g⁻¹.

Table 1. Comparison of the Physical Properties of Methyl Ester with SNI 14-71822006 and ASTM D6751

| Parameter       | Units             | Results     | SNI 04-7182-2006 | ASTM D6751 |
|-----------------|-------------------|-------------|------------------|------------|
| Density         | g.cm⁻³            | 0.8828      | 0.85 – 0.9       | 0.85 – 0.9 |
| Viscosity       | mm².s⁻¹ (cSt)     | 6.431       | 2.3 – 6.0        | 1.9 – 6.0  |
| Acid Number     | mgKOH.g⁻¹         | 0.563       | Max. 0.8         | Max. 0.8   |

4. Conclusion

The results showed that the yield increased with the increase in the mole ratio of methanol: *Jatropha curcas* oil, but the yield decreased when the mole ratio of methanol: castor oil was too large. The results showed that the yield increased along with an increase in temperature, but the yield will decrease if the temperature is too large and exceeds the boiling point of methanol (65°C). The maximum condition for the most abundant biodiesel yield is obtained in the mole ratio of methanol to castor oil of 15:1 (mol/mol) at 65°C for 5 hours was 59.80%. The results showed that the physical properties for density, viscosity, and acid number were in accordance with the quality standards of SNI 14-7182-2006 methyl ester.

5. References

[1] Islam, A., Taufiq-Yap, Y. H., Chu, C.-M., Chan, E.-S., and Ravindra, P., 2013.”Studies on Design of Heterogeneous Catalysts for Biodiesel Production”, Process Safety and Environmental Protection, Vol. 91, pp. 131–144.
[2] Kumar, S.A.A., Sakthinathan, G., Vignesh, R., Banu, J. Rajesh., and Al-Muhtaseb, Ala'a H., 2019, "Optimized transesterification reaction for efficient biodiesel production using Indian oil sardine fish as feedstock”, Fuel, Vol. 253, pp. 921 – 929.
[3] Lee, J.-S. and Saka, S., 2010, “Biodiesel Production by Heterogeneous Catalysts and Supercritical Technologies”, Bioresource Technology, Vol. 101, pp. 7191–7200.
[4] Ab Rahman, N. A., Olutoye, M. A., and Hameed, B. H., 2011, “Synthesis of Methyl Esters from Palm (Elaeis guineensis) Oil Using Cobalt Doped MgO as Solid Oxide Catalyst”, Bioresource Technology, Vol. 102, pp. 9749–9754.
[5] Zabeti, M., Wan Daud, W. M. A., and Aroua, M. K., 2009, “Activity of Solid Catalysts for Biodiesel Production: A review”, Fuel Processing Technology, Vol. 90, pp. 770–777.
[6] Louhasakul, Y., Cheirsilp, B., Maneerat, S., and Prasertsan, P., 2018, “Direct Transesterification of oleaginous yeast lipids into biodiesel: Development Of Vigorously Stirred Tank Reactor And Process Optimization, Biochemical Engineering Journal, Vol. 137, pp. 232 – 238.
[7] Lam, M. K., Lee, K. T. and Mohamed, A. R., 2010, “Homogeneous, Heterogeneous and Enzymatic Catalysis for Transesterification of High Free Fatty Acid Oil (Waste Cooking Oil) to Biodiesel: Areview”, Biotechnology Advances, Vol. 28, pp. 500–518.
[8] Kim, S.K., Brand, S., Lee, H., Kim, Y., dan Kim, J. 2013. Production of renewable diesel by hydrotreatment of soybean oil: Effect of reaction parameters. Chemical Engineering Journal. 228:114-123.
[9] Agarwal, M., Chauhan, G., Chaurasia, S. P. and Singh, K., 2012, “Study of Catalytic Behavior of KOH as Homogeneous and Heterogeneous Catalyst for Biodiesel Production”, Journal of the Taiwan Institute of Chemical Engineers, Vol. 43, pp. 89–94.

[10] Feng, H. Z., Lan, P. Q., and Wu, S. F., 2012, “A Study on the Stability of a NiO–CaO/Al₂O₃ Complex Catalyst by La₂O₃ Modification for Hydrogen Production”, International Journal of Hydrogen Energy, Vol. 37, pp. 14161–14166.