EnviroScienteae Vol. 15 No. 1, April 2019
Halaman 79-85

ISSN 1978-8096 (print)
ISSN 2302-3708 (online)

UTILIZATION OF STEROL GLYCOSIDES IN FAME (*Fatty Acid Methyl Ester*) BYPRODUCTS FROM THE BIODIESEL INDUSTRY

Pemanfaatan Sterol Glikosida Dalam FAME (Fatty Acid Methyl Ester) Hasil Samping dari Industri Biodiesel

Noor Ridha Yanti[1)], Meilana Dharma Putra[2)], Agung Nugroho[3)*], HestyHeryani[3) **]

[1)] Department of Natural Resources and Enviroment Management, Graduate Program, University of Lambung Mangkurat, Banjarbaru 70714, Indonesia
e-mail : ridha.yanti393@gmail.com
[2)] Department of Chemical Engineering, Faculty of Engineering, University of Lambung Mangkurat, Banjarbaru 70714, Indonesia
e-mail : mdputra@ulm.ac.id
[3)] Department of Agro-Industrial Technology, Faculty of Agriculture, University of Lambung Mangkurat, Banjarbaru 70714, Indonesia
* e-mail : agungnug19@gmail.com
** e-mail : hheryani@ulm.ac.id

Abstract

In recent years, the development of renewable energy such as biodiesel has been widely researched throughout the world as technology advances in the era of Industry 4.0. At the final station of biodiesel production in the maturation tank, the by-products will form by-products in the form of sterol glycosides in *Fatty Acid Methyl Esters* which have not been utilized. This study aims to determine the volume of biodiesel from a mixture of sterol glycosides with a ratio of 0.5% H_2SO_4 catalyst concentration; 1%; 1.5% and 2% and tested their characteristics in accordance with the Indonesian National Standard (SNI 7182: 2015). Biodiesel production was carried out by esterification with a molar ratio of 1:6 (sterol glycoside: methanol) to variations in H_2SO_4 catalyst concentration. The results of the highest yield volume biodiesel were obtained from a catalyst concentration of 1.5% of 28.02% and the lowest yield of 17.50% in a 0.5% catalyst. Based on the characteristic test of biodiesel by varying the concentration of catalyst H_2SO_4 obtained density of 852 – 862 kg m^{-3}, viscosity of 4.642 – 4.950 mm^2 s^{-1} and saponification number of 191.007 – 198.164 mg-KOH g^{-1} according to standard characteristics SNI 7182:2015, while for the water content of 0.1965 – 0.1976% and acid numbers of 2.151 – 3.232 mg-KOH g^{-1} isn't according to standard characteristics. Based on research, pre-treatment treatments was recommended before the refining process to reduce the amount of acid and moisture content so according to standard characteristics.

Keywords: biodiesel; esterification; sterol glycosides; sulphuric acid

INTRODUCTION

Currently the manufacturing industry in developing countries, especially Indonesia is very rapidly supported by technological advances with the concept of Industry 4.0 in the production supply chain (Hermann *et al*., 2016; Lasi *et al*., 2014). The biodiesel industry produces products that are environmentally friendly, so that many researchers around the world are interest. In this case, many researchers carried out the development of renewable energy to reduce fossil fuel consumption, biodegradability and reduce emissions of harmful air pollutant (Omar Amin, 2011; Magara-Gomez *et al*., 2012; Songtawee *et al*., 2014).

Biodiesel could be produced from raw materials from vegetable oils and animal fats (Songtawee *et al*., 2014; Hidayatno *et al*., 2015). Biodiesel was produced by transesterification using base catalysts which produced byproducts such as water, free and bounded glycerides, free fatty acids, catalysts, residual alcohols, and unsaponifiable materials (sterols, tocopherols and hydrocarbons) (Wang *et al*, 2010). Sterol glycosides were white precipitate which formed at the final station of biodiesel production, namely tank maturation (Songtawee *et al*., 2014).

Currently sterol glycosides which have been separated from Fatty Acid Methyl Ester (FAME) in the biodiesel industry were only accommodated in conductors and then burned, so that in this case researchers need to use sterol glycosides for alternative fuels (biodiesel) to minimize environmental pollution around the plant. The purpose of this research was to determine the yield volume of biodiesel from the raw material of a mixture of sterol glycosides in fatty acid methyl ester from H_2SO_4 catalyst concentration of 0.5%; 1%; 1.5% and 2% and tested the characteristics according to the Indonesian National Standard (SNI 7182:2015).

MATERIAL AND METHOD

Raw Materials and Chemicals

The sterol glycoside sample in FAME (Fatty Acid Methyl Ester) was taken at the maturation tank in the biodiesel industry. The materials used in the esterification process were methanol (70%, technical), sulfuric acid (H_2SO_4) (95–98%, p.a), distilled water and materials for analysis were solution of hydrochloric acid (HCl) MERCK 0.5 N, indicator phenophtalin (PP) 1%, solution of KOH alcohol 0.5 N and solution of potassium hydroxide (KOH) MERCK 0.1 N.

Method

Initial treatment of the raw material for sterol glycosides in FAME (Fatty Acid Methyl Ester) by preheating to 130 ± 2°C for 30 minutes. Next, filtering samples from the impurity was carried out and left to room temperature (20-25°C).

At the stage of esterification of biodiesel production was modifying the method which carried out by (Tremblay & Montpetit, 2017). Sterol glycosides were reacted with methanol in a three-neck flask equipped with a hot water bath, a condenser, thermometer and magnetic stirrer. The conditions used in this reaction were temperature of 60°C, the ratio of sterol glycosides in FAME/methanol (1:6), stirring speed of 600 rpm, reaction time of 2 hours and variations in sulfuric acid catalyst concentration (H_2SO_4) were 0.5%, 1% , 1.5% and 2% of sterol glycosides's weight. After 2 hours, the reaction results in the reactor were transferred to a separating funnel placed in a 50°C hot water container and left in the phase formation for 3 hours. The upper phase results were put back into the separating funnel to did the washing process with distilled water that had been heated to 55°C in the hot water bath. The water was put into a separating funnel of 15 ml and then let stand for a moment until the water phase is formed at the bottom. The water phase was removed then washed again the upper phase for 5 times. Then the results of the upper phase (methyl ester/biodiesel) were put into a beaker glass and dried in an oven at a temperature of 130 ± 2°C for 30 minutes.

The parameters of the success test for the yield volume of biodiesel products produced in this research were calculated using the following formula (Pannilawithana & Pathirana, 2017):

$$\textbf{Yield (\%)} = \frac{\textbf{weight of biodiesel}}{\textbf{weight of raw oil}}\ \textbf{x 100\%}$$

The biodiesel solution was then analyzed for its characteristics including water content, density, viscosity, acid numbers and saponification number according to the quality of biodiesel (SNI-7182:2015, 2015)

RESULTS AND DISCUSSION

Yield Volume Biodiesel

The esterification results from sterol glycosides in FAME (Fatty Acid Methyl Ester) and methanol with variations in concentrations of 0.5%, 1%, 1.5% and 2% produced bright-yellow methyl ester (biodiesel). This shows that the esterification reaction conditions were successfully carried out into methyl esters. Based on the research, the biggest biodiesel yield was produced on a 1.5% catalyst which was 28.02% and the lowest biodiesel yield was 17.50% which can be seen in Figure 1.

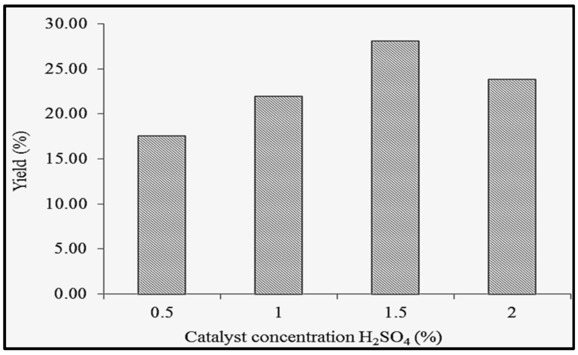

Figure 1. Effect of sulfuric acid (H_2SO_4) catalyst concentration on the volume of biodiesel yield

In Figure 1, the greater concentration of the catalyst in the solution, the activation energy of a reaction got smaller, so that more products would be formed. Increasing the catalyst concentration caused an increase in biodiesel yield. If the concentration of the H_2SO_4 catalyst continued to increase to 2%, the biodiesel yield formed would actually continue to decrease. This happens caused the addition of excessive catalyst concentration, encouraged the reaction of the formation of soap. According to Koh & Ghazi, (2011) The catalyst functions to increase the reaction rate. The more amount of catalyst added will increase the reaction rate.

In addition, the heating operating temperature used 60°C did not exceed the boiling point of methanol (65°C) so that the sterol glucoside and methanol with the addition of a catalyst could be converted into biodiesel. When this temperature was increased to 70°C, past the boiling point of methanol, then a portion of methanol had a phase change from liquid to gas. According to Refaat, (2010) the occurrence of this methanol phase change caused the amount of methanol in the liquid phase to decrease. The reduced amount of methanol in solution caused a reduction in the number of effective collisions to produce biodiesel so that the yield of the biodiesel formed would decrease.

Water content

The results of the biodiesel water content characteristics can be seen in Figure 2, which shows the water content at the catalyst concentration of 1.5% and 2% at 0.1965% lower than the catalyst concentration of 0.5% and 1%. This difference was influenced by the washing treatment in the process of refining alternative fuels. High levels of water in oil could cause the manufacturing process to undergo hydrolysis during the process. According to Banga & Varshney, (2010) Biodiesel water content which was high affected storage because it caused microbes to grow easily so that it polluted biodiesel, corrosion on the engine and at low temperatures caused the separation of pure biodiesel.

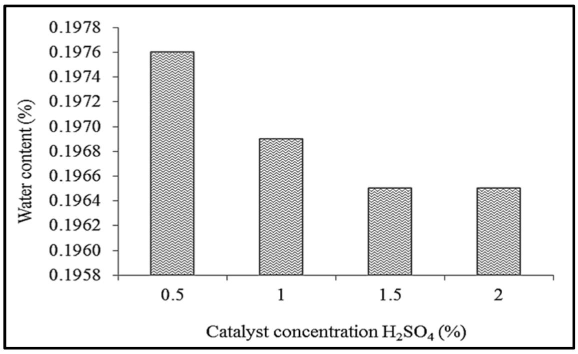

Figure 2. Effect of sulfuric acid (H_2SO_4) catalyst concentration on water content

Density

Density shows the weight ratio of volume per unit. This characteristic is related to the heating value and power produced by diesel engines per unit volume of fuel. Density was influenced by glycerol factors found in methyl esters (FAME) (Chavarria-Hernandez & Pacheco-Catalán, 2014). If biodiesel had a density exceeding the provisions, an imperfect reaction would occur in the conversion of vegetable oils such as increasing engine wear, emissions, and causing damage to the engine. SNI standard for biodiesel density is 850 – 890 kg m^{-3} at temperature of 40°C (SNI-7182:2015, 2015). The result of biodiesel density characteristic can be seen in Figure 3.

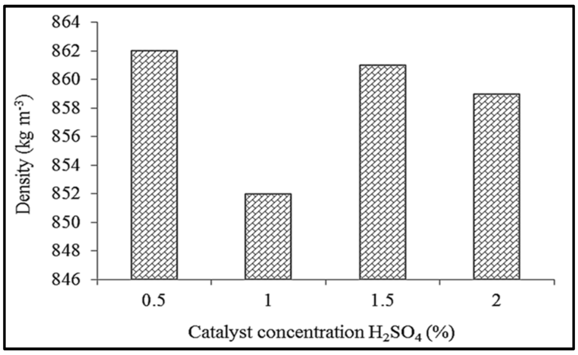

Figure 3. Effect of sulfuric acid (H_2SO_4) catalyst concentration on density

As seen in Figure 3, the highest density was found when the H_2SO_4 concentration of 0.5% was 862 kg m^{-3}, while the lowest density was at 1% H_2SO_4 concentration of 852 kg m^{-3}. This shows that the H_2SO_4 catalyst was able to help the collision of fatty acids that occured in the esterification process would split into methyl esters (biodiesel) so that the density decreased in line with decreasing molecular weight and this value had met the standard biodiesel criteria according to SNI 7182: 2015 on biodiesel quality requirements. According to Chavarria-Hernandez & Pacheco-Catalán, (2014) the greater level of density produced showed that the washing and purification process of methyl esters (biodiesel) was less than perfect.

Viscosity

The viscosity of biodiesel must meet SNI values ranging from 2.3 – 6.0 mm^2 s^{-1}. The value of viscosity which was too high could make the atomization of fuel and air less good, namely combustion became imperfect in the use of biodiesel (SNI-7182:2015, 2015). The results of biodiesel viscosity can be seen in Figure 4.

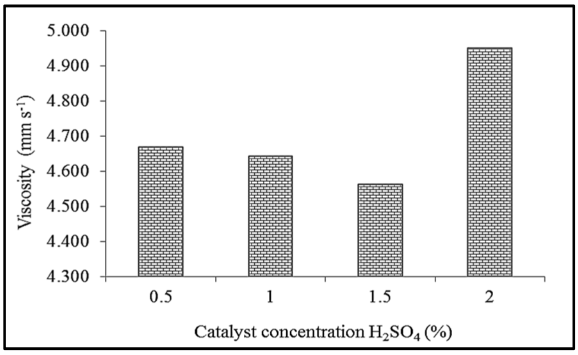

Figure 4. Effect of sulfuric acid (H_2SO_4) catalyst concentration on viscosity

As seen in Figure 4, the concentration of sulfuric acid on the viscosity of biodiesel with the highest kinematic viscosity value at 2% H_2SO_4 concentration was 4.950 mm^2 s^{-1}, while the lowest viscosity was at 1% H_2SO_4 concentration of 4.642 mm^2 s^{-1} and if compared with the quality of biodiesel according to SNI 7182: 2015 concerning the quality requirements of biodiesel, this had met the standard characteristic criteria.

Acid numbers

Sterol glucosides in FAME had an acid number of 5.23. This figure shows that the content of free fatty acids in oil was still very high. With the addition of sulfuric acid catalyst concentrations of 0.5%, 1%, 1.5% and 2% in the esterification reaction, the acid numbers in the sample decreased which can be seen in Figure 5.

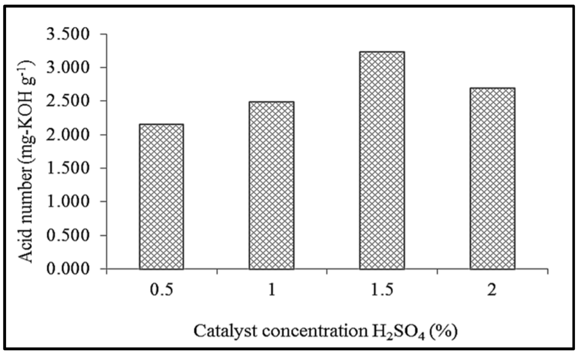

Figure 5. Effect of sulfuric acid (H_2SO_4) catalyst concentration on number of acid

Based on Figure 5, it is known that the acid numbers of the biodiesel produced from the sterol glucoside esterification reaction and methanol with the addition of 0.5% H_2SO_4 catalyst could reduce the acid number to low of 2.151 mg-KOH g^{-1}, while the addition of 1.5% H_2SO_4 catalyst was only able to reduce acid numbers to 3.232 mg-KOH g^{-1} compared to 1% H_2SO_4 catalyst of 2.487 mg-KOH g^{-1} and 2% H_2SO_4 catalyst of 2.695 mg-KOH g^{-1}. This shows that the increasing concentration of catalyst H_2SO_4 which was increasing caused the acid number to be higher. This value was still beyond the quality standard set by SNI-7182:2015, (2015), the acid number was a maximum of 0.5 mg-KOH/g still not fulfilling the number of acid numbers from the biodiesel produced, was possible because the levels of free fatty acids in the initial glucoside sterols were still high. The esterification process carried out had not been effective enough to reduce the total acid level in the biodiesel produced, so it needs to be purified with absorbent materials, namely activated carbon. Fadhil *et al*., (2012) refined biodiesel using activated carbon produced from used tea waste and obtained crude methyl ester by 97%. This was because adsorption occured through physical or chemical interactions between the surface of the adsorbate and the surface of the activated carbon adsorbent which had a high surface area.

Saponification number

The saponification number shows the amount of mg-KOH needed to do saponification 1 gram of sample (Kumar, 2014). The soap contained was the remnants of esterification and minerals which were not neutralized totally. The saponification number obtained from the esterification of sterol glucoside and methanol reaction with the addition of 0.5% H_2SO_4 catalyst was 191.851 mg-KOH g^{-1}, addition of 1.5% H_2SO_4 catalyst for 197.002 mg-KOH g^{-1}, 1% H_2SO_4 catalyst for 198.164 mg-KOH g^{-1} dan 2% H2SO4 catalys for 191.007 mg-KOH g^{-1} which can be seen in Figure 6.

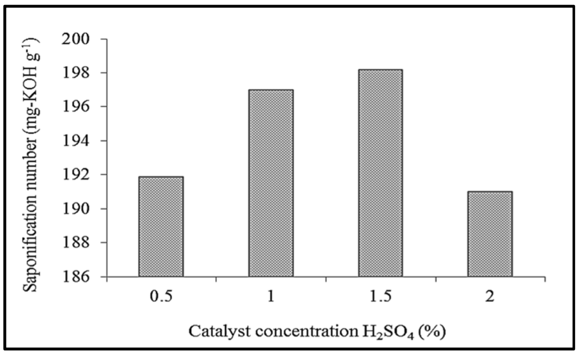

Figure 6. Effect of sulfuric acid (H_2SO_4) catalyst concentration on saponification number

From Figure 6, shows the results of calculations according to SNI-7182:2015, (2015) that biodiesel saponifiaction number from each sample were in accordance with the requirements for biodiesel quality of <500. According to Raqeeb & Bhargavi, (2015) the smaller the saponification value, the good product produced.

CONCLUSION

From the results of the research can be concluded as follows :

1. The more concentration of H_2SO_4 catalyst added to the esterification process will affect the volume yield of the biodiesel produced.

2. At 1.5% H_2SO_4 catalyst concentration produced the highest biodiesel volume yield was 28.08%.
3. Based on the characteristic test of biodiesel on variations in H_2SO_4 concentrations obtained a density of 852 – 862 kg m^{-3}, the viscosity was 4,642 – 4,950 mm^2 s^{-1} and saponification number was 191,007 – 198,164 mg-KOH g^{-1} which had met SNI 7182: 2015 criteria.
4. Pre-treatment before the refining process can be recommended to reduce acid numbers and water content so that they meet the standard characteristics.

ACKNOWLEDGEMENTS

The authors thank the Graduate Program at Lambung Mangkurat University for supporting the work.

REFERENCES

Banga, S & Varshney, P K. (2010). Effect of impurities on performance of biodiesel: A review.

Chavarria-Hernandez, J C & Pacheco-Catalán, D E. (2014). Predicting the kinematic viscosity of FAMEs and biodiesel: Empirical models. *Fuel, 124*: 212-220.

Fadhil, A B., Dheyab, M M., & Abdul-Qader, A -Q Y. (2012). Purification of biodiesel using activated carbons produced from spent tea waste. *Journal of the Association of Arab Universities for Basic and Applied Sciences, 11*(1): 45-49.

Hermann, M., Pentek, T., & Otto, B. (2016). *Design principles for industrie 4.0 scenarios.* Paper presented at the System Sciences (HICSS), 2016 49th Hawaii International Conference on.

Hidayatno, A., Sutrisno, A., Zagloel, Y M., & Purwanto, W W. (2015). System dynamics sustainability model of palm-oil based biodiesel production chain in Indonesia. *International Journal of Engineering and Technology (IJET), 15*(06): 20-26.

Koh, M Y & Ghazi, T I M. (2011). A review of biodiesel production from Jatropha curcas L. oil. *Renewable and sustainable energy reviews, 15*(5): 2240-2251.

Kumar, A. (2014). Physico-chemical and natural products investigations of essential oil from the rhizomes of Kaempferia galanga L. *Der Chem Sinica, 5*(2): 91-94.

Lasi, H., Fettke, P., Kemper, H -G., Feld, T., & Hoffmann, M. (2014). Industry 4.0. *Business & Information Systems Engineering, 6*(4): 239-242.

Magara-Gomez, K T., Olson, M R., Okuda, T., Walz, K A., & Schauer, J J (2012). Sensitivity of hazardous air pollutant emissions to the combustion of blends of petroleum diesel and biodiesel fuel. *Atmospheric Environment, 50*: 307-313.

Omar, W N N W & Amin, N A S. (2011). Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and bioenergy, 35*(3): 1329-1338.

Pannilawithana, N A & Pathirana, H M. (2017). A green method to produce biodiesel from palm olein oil. *Journal of Oil Palm Research*, *29*(2): 267-277.

Raqeeb, M A & Bhargavi, R. (2015). Biodiesel production from waste cooking oil. *Journal of Chemical and Pharmaceutical Research, 7*(12): 670-681.

Refaat, A. (2010). Different techniques for the production of biodiesel from waste vegetable oil. *International Journal of Environmental Science & Technology, 7*(1): 183-213.

SNI-7182:2015. (2015). Indonesian National Standard (SNI) 7182: 2015 about Biodiesel Quality Terms. *Jakarta. National Standardization Agency*.

Songtawee, S., Ratanawilai, S., & Tongurai, C. (2014). Effect of Sterol Glucosides in Biodiesel Production. *International Journal of Advances in Chemical Engg., & Biological Sciences (IJACEBS), 1*: 1507-1515.

Tremblay, A Y & Montpetit, A. (2017). The in-process removal of sterol glycosides by ultrafiltration in biodiesel production. *Biofuel Research Journal, 4*(1): 559-564.

Wang, H., Tang, H., Salley, S & Ng, K. S. (2010). Analysis of sterol glycosides in biodiesel and biodiesel precipitates. *Journal of the American Oil Chemists' Society, 87*(2): 215-221.