QUALITY ANALYSIS OF BIODIESEL FROM PALM OIL

Rahmawati[1], Alfian Noor[2], Maming[2], Muhammad Zakir[2]

[1]Postgraduate of Chemistry University of Hasanuddin, Makassar
[2]Departement of Chemistry, Faculty of Sciences, University of Hasanuddin, Makassar
Contact: Rahmawatiamma60@gmail.com

Abstract

Biodiesel (fatty acid methyl esters or FAME) an alternative fuel to substitute diesel oil or diesel fuel made from oils or fats of vegetable or animal. Oils commonly used for biodiesel fuel, among others palm oil. Biodiesel is produced through the transesterification of oils or esterification of fatty acids. The research objective was to determine the quality of biodiesel from palm oil reflux results through the process of esterification and transesterification. Transesterification reaction is the formation of esters and glycerol from trigliserin (fat/oil) with methanol. Transesterification is a type of equilibrium reaction (reversible, where the addition of NaOH catalyst (chemical catalysts) can accelerate the achievement of a state of equilibrium. The results showed that rendamen biodiesel was obtained by 77% and quality parameters that defined American Society for Testing and Materials (ASTM D6751) has meet the standards in terms of density of 0.8654 g/mL, saponification 5.2979 mg KOH /g of oil, iodine number 18.9184 g I2/100g.

Keywords: Quality, biodiesel, palm oil

1. INTRODUCTION

The use of fuel that is continuous and is likely to increase due to growth in population and industry, while oil reserves are dwindling and can not be renewed, potentially causing an energy crisis in the future. Therefore, to solve this problem and reduce the dependency on oil should be a diversified energy by looking for alternative renewable energy (renewable). One is alternative energy derived from oil crops / plants [15].

One type of renewable energy is biodiesel. As part of a package of economic policy, the government will try to increase the portion of biodiesel in the sale of biodiesel. The government will revise the regulation of the Minister of Energy and Mineral Resources No.32 of 2008 concerning the use, procuring, and the marketing of biofuels, with the aim to increase levels of biodiesel blends in biodiesel by 10% from the previous 5% [8].

Biodiesel is an alternative fuel for motor vehicles fueled by diesel oil. Biodiesel can be produced from palm oil, soya and jatropha. In the development of biodiesel, the main raw material is still used is oil derived from palm oil. Palm oil is a potential source of energy. As a country with fertile land, Indonesia has a huge potential to play a role in the oil palm industry. Given the oil palm is a plant commonly grown and enough potential to be developed in Indonesia, so that with the increase in oil demand in the transport sector resulted diesel alternative fuel mixing biodiesel and diesel oil in Indonesia can be pursued [4]. Therefore, research was conducted to determine the quality of biodiesel from palm oil, which can be used for alternative fuels, so as to overcome the scarcity of fuel in the future.

Biodiesel is an effort to prevent human dependence on diesel fuel for diesel engines [5]. Biodiesel is a promising substitute for fossil fuels because it comes from renewable energy sources. Biodiesel can be obtained through the transesterification of triglycerides from vegetable oils and fats or animal with a short chain mono-alcohol (usually methanol or ethanol) in the presence of a catalyst, to produce a mixture of ethyl or methyl ester (biodiesel) together with the byproduct, glycerin [13].

Methanol can produce more than the ester of ethanol and butanol. Methanol is a type of alcohol that is widely used for the transesterification process because it is more reactive and can produce biodiesel equal to the use of ethanol is 1.4 times more compared to methanol [2].

The catalyst in the production process of biodiesel is a material that serves to accelerate the reaction by lowering the activation energy (activation energy, Ea). The production process will be very slow and requires high temperature and high pressure without the use of a catalyst [6].

If the oil has a value of FFA <0.5%, it can be directly processed by transesterification with a base catalyst, if the FFA content of>5% then the process should be carried out with Ice-trans (esterification-transesterification). An acid catalyst is used in order to synthesize the oil that has a high FFA values. An acid catalyst is done in order to synthesize the oil that has a high FFA values. Acid catalyst such as sulfuric acid, phosphate acid, hydrochloric acid suitable for the reactions that have high free fatty acid value [17].

Transesterification reaction using an alkaline catalyst is influenced by several factors, namely internal and eksernal. Internal factors are the quality of the raw material of oil itself as well as the water content of free fatty acids which adversely affects the reaction. External factors is the mole ratio between alcohol and oil, the type of catalyst, reaction time, temperature, and other parameters after transesterification. NaOH is a base catalyst which is widely used in comparison with acidic catalysts such as KOH, it is because the metal Sodium (Na) has a higher reactivity than potassium (K) [11]. The percentage of NaOH as much as 0.6% to 20% methanol to produce maximum ester yield is equal to 87.3% [9].

2. RESEARCH METHODS

2.1 Materials Research

The materials used in this study are palm oil, methanol, H_2SO_4, NaOH, HNO_3 65 %, KOH 0,1 N, HCl 37 %, $Na_2S_2O_3.5H_2O$, $H_2C_2O_4.2H_2O$, KIO_3, $Na_2B_4O_7.10H_2O$, KI 10%, indicators phenolphthalein indicator MO, starch, distilled water, diesel, and biodiesel.

2.2 Research Tools

The tools used in this research is the balance of digital, pipette, beaker, stirrer, measuring cups, 100 mL volumetric flask, pipette volume 25 mL, filter paper, oven, hot plate magnetic stirrer, erlenmeyer 250 mL, cooling behind, neck flask three, watch glass, pycnometer, burette 50 mL, and separating funnel.

2.3 Research Procedure

2.3.1 Synthesis of Biodiesel from Palm Oil

Palm oil is prepared 100 mL. Subsequently, 1.5 mL H_2SO_4 solution dissolved in 25 mL of methanol until homogeneous (solution 1). Then palm oil and 1 mixed solution gradually at a temperature of 70 ºC for 30 minutes. The mixture was added to funnel to the process of separation between biodiesel and glycerol. In the funnel formed two separate phases, namely biodiesel and triglycerides were dilapisan above as well as methanol and glycerol are dilapisan below. The bottom layer was removed and the top layer was continued for leaching. Washing is done by using warm water.

Continue the process of transesterification by reacting back 25 mL of methanol with 1.5 g NaOH at a temperature of 60 °C for 1 hour. After the esterification reaction, do the washing process II, which aims to throw the soap formed, impurities and residual methanol resolve the reaction. Then followed the second separation process is carried out at a temperature of 55 °C, by entering into a funnel where the top layer of the biodiesel and the bottom layer is the remainder of glycerol and methanol. The next stage of purification or drying by heating the biodiesel up to a temperature of 130 °C for 10 minutes.

2.3.2 Analysis of Physical Properties of Biodiesel

2.3.2.1 Biodiesel Density Analysis

The procedure is based on ASTM Method D1475. Determination of density of biodiesel at a temperature of 40 ºC using a pycnometer. Empty pycnometer that has been cleaned and dried and then weighed using the analytical balance. Distilled water that has been heated to a temperature of 40 ºC put into the pycnometer to the brim and then diimpitkan and the temperature is recorded. The outer walls are dried pycnometer. Then pycnometer containing distilled water are weighed and the weight recorded. Distilled water is then replaced with biodiesel to be measured which has been heated at 40 °C. Previously, Pycnometer cleaned and dried. The weighing results recorded. The above procedure is repeated as many as two (2) times.

Calculation of biodiesel density (g/cm^3) can be determined using the equation:

$$d_4^t = S_g^t \text{ x } d_{aq}^t \text{ (t ºC)}$$

Where S_g^t is obtained from:

$$S_g^t = \frac{\text{weighted biodiesel}}{\text{weight of distilled water}}$$

2.3.3 Analysis of biodiesel chemical properties

2.3.3.1 Analysis of Free Fatty Acid levels (Free Fatty Acid)

The analysis procedure is based on the AOCS Method Ca 5a-40 is ± 7.5 g of sample was added to a 100 mL Erlenmeyer flask, add 50 ml of 95% neutral alcohol and then heated in a water bath until a homogeneous solution is formed. Once cooled then titrated with 0.1 N KOH using phenolphthalein indicator. Calculated levels of free fatty acids.

Calculation of free fatty acid content (%) can be determined using the equation:

$$\text{\% free fatty acids} = \frac{\text{N KOH x V KOH x 25,6}}{\text{sample weight}} \%$$

2.3.3.2 Analysis of saponification

The analysis procedure is based on AOCS Method Cd 3-25 is a sample of ±0.5 g inclusion in a 100 mL Erlenmeyer flask, then added 50 mL of 0.5 N alcoholic KOH. Furthermore boiled until completely saponified oil is characterized by the apparent absence of grains of fat or oil in the solution. Once cooled then titrated with 0.5 N HCl using phenolphthalein indicator. The end point of the titration properly marked loss of red color.

Calculation of saponification (mg/g) can be determined using the equation:

Saponification =

$$\frac{\text{V HCl}_{blank} \text{ x V HCl}_{sample}}{\text{sample weight}} \text{ x N HCl x 56,11}$$

2.3.3.3 Analysis of Iodine Numbers

Iodine number is determined by titration. Biodiesel as much as ± 0.2 g inclusion in a 100 mL Erlenmeyer flask and add 5 mL of HCl 5%, stirring until homogeneous and then covered with aluminum foil and simmer for 1 minute. After cooling, 0.05 M iodine solution was added to a solution of 15 mL and then closed immediately and shaken then titrated with sodium thiosulfate solution until a yellowish then added 2-3 drops of 1% starch solution and the titration is continued until colorless. Penitar solution volume is recorded and is given a numerical value iodine.

Iodine number calculation can be determined using the equation:

$$\text{Iodine number} = \frac{\text{(Vb – Vs) x N } Na_2S_2O_3 \text{ x BE Iod}}{\text{Sample weight (mg)}} \text{ x}$$

100

3. RESULTS AND DISCUSSION

3.1 Esterification process results

The mechanism of esterification reaction consists of several stages, namely the transfer of protons from the acid catalyst to the oxygen atom of the carbonyl thereby increasing elektrofilisitas of carbon atoms carbonyl carbon atom of the carbonyl is attacked by oxygen atoms of the alcohol that is nucleophilic forming oxonium ion, the release of a proton from the hydroxyl group of alcohol produce complex activated, and protonated against one hydroxyl group followed by the release of water molecules to produce ester.

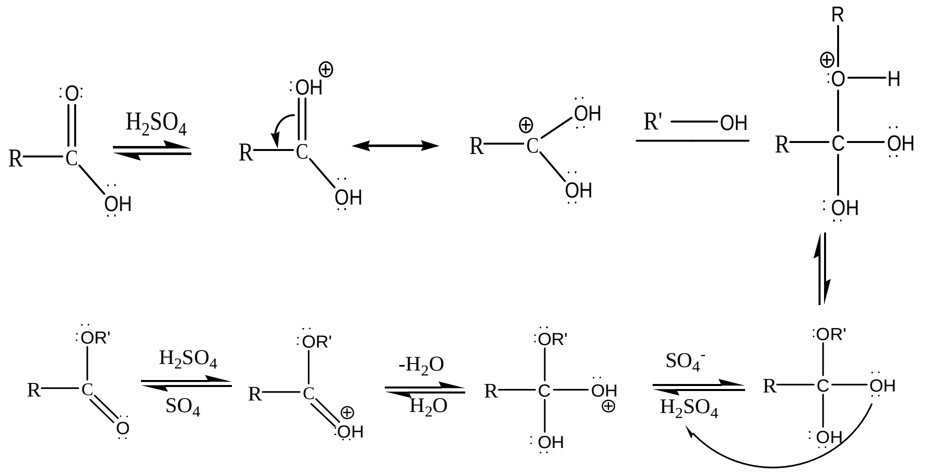

Figure 1. Reaction Mechanism esterification with sulfuric acid catalyst [7].

3.2 Results transesterification process

Biodiesel synthesis process can be done in three stages namely the reaction of esterification and transesterification reactions. Phase esterification done to reduce levels of free fatty acids in the oil. Oil esterified with methanol at a catalyst H_2SO_4, heated at a temperature of 60 ºC with a time of 60 minutes. The results of the esterification reaction was treated again with methanol and sodium hydroxide as a catalyst, is heated at a temperature of 60 ºC with a time of 60 minutes, the reaction that occurs is a transesterification reaction. Transesterification reaction mechanism is as follows:

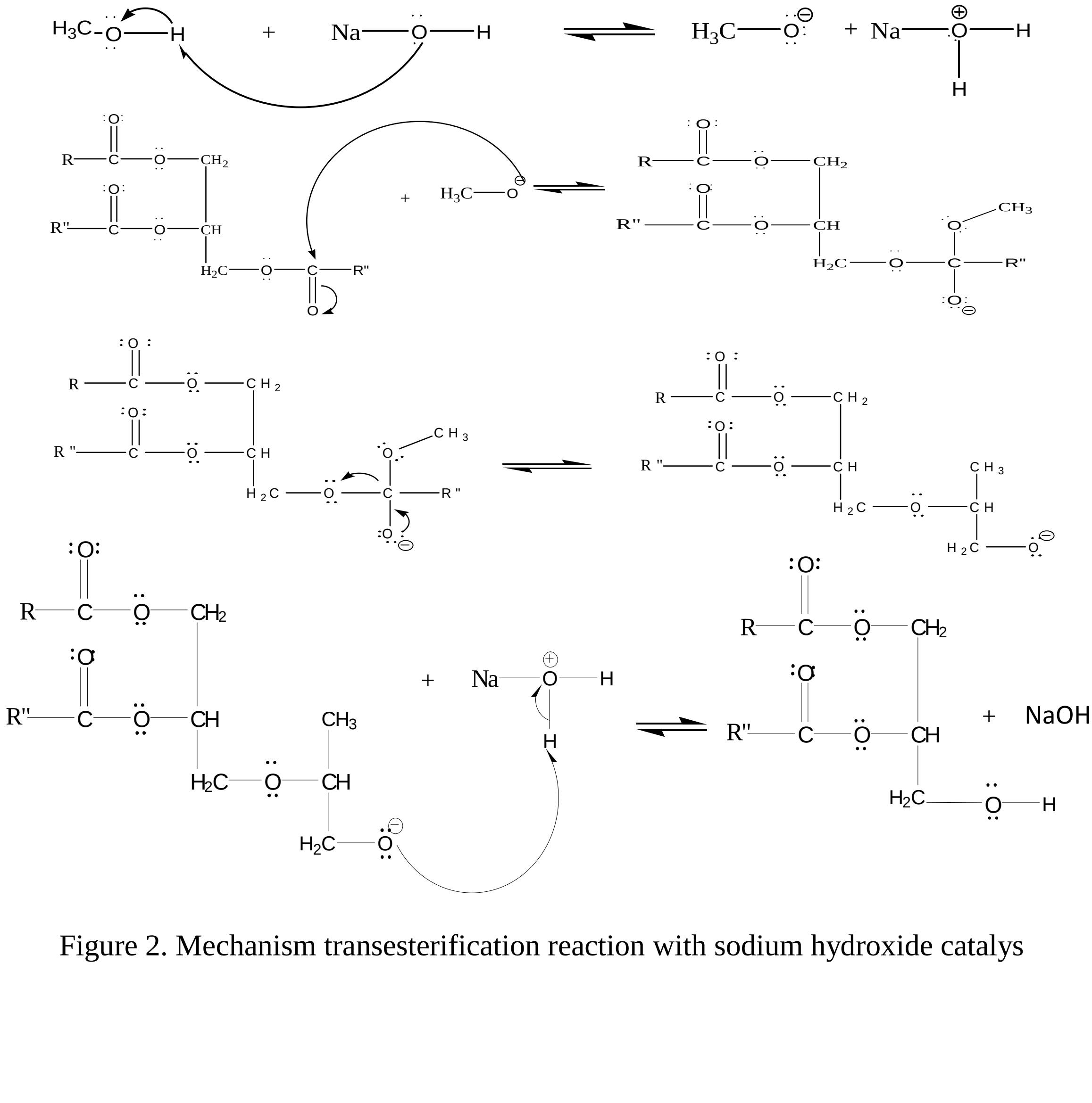

Figure 2. Mechanism transesterification reaction with sodium hydroxide catalys

3.3 Analysis of physical properties of biodiesel

The result of the synthesis of biodiesel from mrlalui esterification and transesterification reaction is then carried out the characterization of physical properties based on the standard ASTM D6751. Physical properties of biodiesel includes the analysis of the density and viscosity.

3.3.1 Biodiesel density analysis

Results of analysis of the density of biodiesel obtained at 0.8654 g/cm^3.40 ºC standard density values specified in ASTM D6751 is 0.82 to 0.90 g/cm^3. The results obtained can be said to be included in the range of density values that have been set. The density of biodiesel is dependent on fatty acid composition and purity. Density increases with decreasing chain length of the growing number of double bonds. Another thing that causes the density the greater is the increasingly high reaction temperature and a greater concentration of basic catalyst due to the use of high temperature and catalysts excess transesterification reactions will improve the reaction of saponification that substances impurities such as soap, potassium and glycerol formed causes the density of biodiesel into greater than. On the other hand, the density can be reduced by the presence of contaminants such as methanol [16].

Density is one determinant of the quality biodiesel because it is associated with calorific value and the generated power diesel engines. The lower the density values, the calorific value or the burning will also be higher [3]. If biodiesel has the density exceeds the provisions will result in engine wear, emissions, and cause damage to the engine [14].

3.4 Analysis of biodiesel chemical properties

Test chemical properties of biodiesel is based on ASTM D6751 standard includes the analysis of the levels of free fatty acids (% FFA), saponification and iodine numbers.

3.4.1 Analysis of Free Fatty Acid levels (Free Fatty Acid) biodiesel

Analysis of free fatty acid content of biodiesel is based on analysis method AOCS Ca 5a-40. Results of free fatty acid content of biodiesel obtained at 6.6048%. Standard levels of free fatty acids (% FFA) biodiesel recommended in ASTM D6751 is a maximum of 0.4500%. Free fatty acid research results do not meet the parameters set by ASTM D6751. Free fatty acid levels are high can lead to deposition in the combustion system, the higher the free fatty acids, the lower the quality of diesel fuel. High free fatty acid can also reduce the life of the pump and filter.

3.4.2 Analysis of saponification biodiesel

Analysis carried out by saponification AOSC method Cd 3-25. The results obtained by saponification of biodiesel amounted to 5.2979 mg KOH/g. Saponification biodiesel standards set forth in ASTM D6751 is a maximum of 500 mg KOH/g. The results obtained can be said to meet the quality standards specified saponification.

Saponification is defined as the number of milligrams of KOH required to menyabunkan one gram sample. Saponification depends on the molecular weight and the percentage concentration of fatty acids contained in the oil or biodiesel. The lower the molecular weight, the higher the saponification, vice versa [12].

3.4.3 Iodine Numbers Analysis biodiesel

Numbers iodine is the amount (grams) of iodine that can be bound by 100 grams of fat. The double bond contained in the unsaturated fatty acid will react with iodine or iodine compounds. Numbers indicate the level of iodine in biodiesel jenuhan lack the building blocks of biodiesel [10].

Results obtained biodiesel iodine number of 18.9184 g $I2/100$ g, these results meet the quality standards of ASTM D6751 iodine number that is not more than 115 g $I2/100$ g. Biodiesel with high iodine numbers will produce ester with power flow and solidification at low temperatures.

Biodiesel has a high degree of non jenuhan not suitable for use as biodiesel as unsaturated molecules will react with oxygen from the atmosphere and converted into peroxide and result in crosslinking in the unsaturated and cause biodiesel polymerized to form a similar plastic material, especially if the temperature increases. As a result the diesel engine will be damaged [1].

4. CONCLUSION

Based on the research results can be concluded that the potential of palm oil as a raw material for making biodiesel. The quality of biodiesel produced in compliance with the defined quality standards of the American Society for Testing and Materials (ASTM D6751) in terms of density of 0.8654 g/mL, saponification 5.2979 mg KOH /g of oil, iodine number 18.9184 g I2/100g, and rendamen 77% biodiesel.

BIBLIOGRAPHY

[1] Azam, M. M., Waris, A. N., dan Nahar, M. (2005). "Prospects and Potential of Fatty Acid Methyl Esters of Some Non-Traditional Seed Oil for Use as Biodiesel in India". Biomass and Bioenergy. 29, 293-302.

[2] Aziz, Islami. 2007. Oil Transesterification Reaction Kinetics. Valensia, Vol. 1, No. 1.

[3] Aziz, I., Nurbayati, S., dan Ulum, B., 2011, Biodiesel Product Manufacture of Cooking Oil Alternative Esterification and Transesterification, Valensia, **2** (3): 443-448.

[4] Boedoyo. M. S. 2006. Mixing Process Technology Biodiesel and Diesel Fuel in indonesia. Prospects for Development of Biofuel as the Substitution of Fuel Oil. 51−61.

[5] Darmawan, F.I., dan Susila, I.W., 2013, Production Process Biodiesel From Used Cooking Oil With Washing Method Dry-Wash System, *JTM*, **2** (1): 80-87.

[6] Darnoko, D, Cheryan M., 2000. Kinetics of Palm Oil Transesterification in Batch Reactor. *J. Am. Oil Chem. Soc.* **77**:1263-1237.

[7] Fessenden, R. J., Fessenden, J. S. 1999, *Organic Chemistry*, Volume 1, Third Edition, Publisher Erlangga, Jakarta

[8] Gunawan, H., 2013, Mandatory biodiesel can plus 20 percent, www. Tribunnews.com/bisnis (accessed 29 Januari 2016).

[9] Hendra, Djeni. 2014. Making Biodiesel From Oil Kemiri Sunan. *Forest Products Research* Vol. 32 No. 1, Maret: 37-45.

[10] Knothe, G., 2005, Dependence of Biodiesel Fuel Properties on The Structur of Fatty Acid Alkyl Esters, Fuel Proc. Technol, **86**: 1059-1070.

[11] Maulana, Farid. 2011. The use of NaOH catalyst in the transesterification process Kemiri Oil into Biodiesel. Journal of Chemical Engineering and the Environment Vol. 8, No. 2, page. 73 – 78.

[12] Nirwana, I.H.S., 2012, Effect of Stirring Speed Process of Making Biodiesel Oil (Jatropha curcas L) by Using Catalyst Abu Bunches Palm, Research Institute, University of Riau, Riau.

[13] Pinto, A.C., Guarieiro, L.L.N., Rezende, M.J.C., Ribeiro, N.M., Torres, E.A., Lopes, W.A., Pereira, P.A.P., and Andrade, J.B., 2005, Biodiesel: An Overview. J. Braz. Chem. Soc., **16**: 1313–1330.

[14] Prihandana, R., Hendroko, R., dan Nuramin, M., 2006, Produce Biodiesel Offers: Overcoming Pollution and Fuel Scarcity, Agromedia Pustaka: Depok.

[15] Sibuea dan Posman, 2003, Biodiesel Oil Industry Development, www.kcm.com, 10 October 2015

[16] Suratno, W., Jumanda, I.K., dan Karlina, R.R., 2007, Methanol Recovery Process Oil Biodiesel from Jatropha (Jatropha curcas oil), National Conference, University of Padjadjaran, Yogyakarta.

[17] Van Gerpen, Jon. 2004. Biodiesel Production and Quality. Department of Biological and Agricultural Engineering. University of Idaho. Moscow