World Chemical Engineering Journal Vol.4, No.2, (2020), pp. 56 – 61

WCEJ

WORLD CHEMICAL ENGINEERING JOURNAL

Journal homepage: http://jurnal.untirta.ac.id/index.php/WCEJ

The Effect of NaOH Catalyst Ratio on Biodiesel Manufacturing from Off Grade CPO

Rudi Hartono[1*], Muklis [1], Wisnhu Pamungkas[1]

[1]Chemical Engineering Department ,Universitas Sultan Ageng Tirtayasa-Indonesia
Jln.Jendral Sudirman Km.3 Cilegon 42435, Indonesia

*Corresponding Author Email:rudi.hartono@untirta.ac.id

ARTICLE HISTORY

Received September 6, 2020
Received in revised form October 11, 2020
Accepted December 19, 2020
Available online December 20, 2020

ABSTRACT

Biodiesel is a type of alternative diesel fuel produced through the esterification and/or transesterification process of plant oils or animal fats. Previous studies state biodiesel preparation by esterification reactions when the content of free fatty acids in vegetable oil raw materials is greater than 2%. However, the biodiesel preparation is conducted by transesterification, If the content of free fatty acids is smaller than 2%. The research aim was to find out the optimum operating conditions of biodiesel manufacturing from low grade CPO as raw materials using the esterification and transesterification process. The research steps were the analysis of low grade CPO raw materials, the esterification process with H_2SO_4 catalyst, and the transesterification process with NaOH catalyst. Fixed variables in the esterification study were oil volume, 1% of H_2SO_4 catalyst, mole ratio of oil and methanol 1:6, reaction time and reaction temperature of 60 ^oC. Whereas, the fixed variables in the transesterification process study were NaOH catalyst ratios of 0.5%, 1% and 1.5%. The produced oil analysis included the content of free fatty acids, density, viscosity, and water content. The physical and chemical properties of low grade CPO were water content of 0.042% and free fatty acids of 49.03. Optimum operating condition of transesterification process was obtained by NaOH catalyst ratio of of 1% which resulted in methyl ester yield of 60.80%. furthermore, the resulting methyl ester had a viscosity value of 5,381 cSt, a density of 870 kg/m^3, an acidic content of 0.11 %, and a water content of 0.028 %.

Keywords: biodiesel, low grade CPO, esterification, NaOH catalyst , transesterification

1. INTRODUCTION

Although as one of the petroleum producing countries, Indonesia is still importing raw materials from abroad. Indonesia's import in September 2019 reached US$ 14.26 billion, an increase of 0.63% compared to imports in August 2019. Cumulatively the value of Indonesia's import reached US$ 126.12 billion (Central Bureau of Statistics 2019). Oil consumption in Indonesia covers transportation, industry, and power generation. Currently the number of diesel-engined devices and vehicles from year to year is increasing. In line with the increase, the fuel needs of diesel engines, namely diesel, have also increased. Another problem that arises from the use of diesel fuel is environmental pollution. Alternative energy sources for diesel fuels that produce more environmentally friendly combustion emissions and do not increase the accumulation of CO_2 gas in the atmosphere are indispensable, thus reducing the effects of global warming.

Biodiesel is produced through transesterification reactions from plant oils, animal fats, and from used oils with methanol by using catalysts to produce fatty acid methyl esters (FAME). Biodiesel can be used as an additive material in petroleum fuels especially for petrodiesel (PD) known as diesel, commonly applied as

20% of biodiesel in diesel mixtures, known as B20. Biodiesel has an advantage over petrodiesel in reducing waste emissions, can be described, has a high flash point, large lubrication and renewable sources. Biodiesel has a high oxygen content from petrodiesel, so its application in diesel engines will show reduction in particulate emissions, carbon monoxide (CO), sulfur, polyaromatic, hydrocarbon (HC), smoke, and noise (Kattimani et al., 2014).

Indonesia is one of the countries that has abundant biodiversity and has great potential as a biodiesel alternative raw material. In Indonesia, there are several plants that have the potential to be developed as biodiesel raw materials, one of which is palm oil or *Elaeis Guineensis*. The greatest potential of Palm Oil plants is in fruits consisting of seeds and shells (skins). On the skin of the fruit is able to produce oil by 30% to 40%-b. This oil can be processed into biodiesel and used as an alternative energy source for solar replacement (Soerawidjaja, 2006). Some researchers who have conducted research on biodiesel from low grade cpo are: Hayyan et al., (2011) conducted biodiesel manufacturing research on the effect of sulphuric acid catalyst concentration, mole ratio, temperature, and stirring rate to reduce free fatty acid (FFA) in CPO trench. FFA levels decreased from 23% to <2% at a catalyst concentration of 1% wt, the oil-methanol mole ratio was 1:12, the stirring rate was 400 rpm, and the temperature was 60^0C. Maulana et al., (2014) conducted research using membrane reactors from off grade CPO under followed operation condition: reaction time of 2 hours, temperature of 60^0C, catalyst concentration of 1 % oil weight, oil mole ratio- methanol 1:12, 1:16, 1:20, and transmembrane pressure ± 1 bar, ± 1.5 bar and ± 2 bar. It yielded of 71.51% on oil mole ratio operating conditions - 1:20 methanol and 2 bar membrane pressure. Syarfi et al,. (2010) conducted biodiesel manufacturing research from CPO trench with a molar ratio of 1:5, process temperature at 60^oC with H_2SO_4 catalyst and biodiesel yield of 89.2%.

The purpose of this study is to analyze the physical and chemical properties of low grade CPO raw materials by concerning at the effect of process stages on the percentage reduction of free fatty acid reduction by means of esterification stage I and esterification stage 2 using acid catalyst. Esterification Phase 1 uses 1% sulfuric acid catalyst (H2SO4) by volume of oil, carried out at a temperature of 60^0C for 90 minutes, if the free fatty acid content is still high above 2% then stage 2 esterification is carried out to reduce the acid number. The second esterification process is the repetition of esterification process stage 1 process and knows the effect of the NaOH catalyst ratio on the transesterification process on the yield of biodiesel products.

2. METHODS

The research was conducted in the Laboratory of Product Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University. The manufacture of biodiesel from low grade CPO was carried out by esterification and transesterification process. The research was conducted in two phases, preliminary research was to determine the effect of sulphuric acid catalyst ratio (H_2SO_4) on the reduction of low grade CPO-free fatty acid content in the esterification process and the follow-up research was to determine the effect of sodium hydroxide catalyst ratio (NaOH) on methyl ester yield in the transesterification process.

2.1 Analysis of physical and chemical properties of off-grade CPO

The study began with an analysis of the physical and chemical properties of low grade CPO raw materials. The initial properties of CPO were important to determine the esterification process. The optimum operating conditions obtained in the initial research became variables in the process of esterification I and esterification II. The transesterification process was carried out after the esterification process. Methyl ester obtained was then analyzed by taking parameters of acid number, density, viscosity and water content.

2.2 Study the effect of sulphuric acid catalyst ratio (H_2SO_4) in the esterification process

Preliminary research was conducted to determine the effect of sulphuric acid catalyst ratio (H_2SO_4) on the reduction of low grade CPO-free fatty acid content in the esterification process. The reactants used were methanol and sulphuric acid catalyst (H_2SO_4).

Firstly, the CPO was melted by heating at 130 ^{o}C for 10 minutes. Then, amount of 250 mL of CPO oil was incorporated into a three-neck flask equipped with condensers, thermometers, and sampling channels. In the three-neck round flask, H_2SO_4 was mixed with methanol with a molar ratio of 1: 6. The addition of H_2SO_4 catalysts according to variations of 0.5, 1, and 1.5%. A methoxide solution, that was a mixture of methanol and H_2SO_4, was inserted in the three-neck round flask containing CPO oil. Temperature reaction was kept constant at 60 ^{o}C, reaction time for the esterification process was 90 minutes. The produced oil was purified from excess methanol and water as a byproduct by heating at 130 ^{o}C for 10 minutes followed by cooling down. Analysis of the free fatty acids content was performed to observe the decrease the of free fatty acids content in low grade CPO.

2.3 Biodiesel production

2.3.1 The Esterification I Process

In the esterification I process of low grade CPO used methanol as reactants and sulphuric acid catalyst (H_2SO_4).

Firstly, the off-grade CPO was melted by heating at 130 °C for 10 minutes. About 250 ml of CPO oil was incorporated into a three-neck flask equipped with condensers, thermometers, and sampling channels. In the three-neck round flask, H_2SO_4 was mixed with methanol with a molar ratio of 1: 6 with H_2SO_4 catalyst as much as 1% of oil volume. A methoxide solution that is a mixture between methanol and H_2SO_4 was inserted in a three-neck flask containing CPO oil. Temperature reaction was kept constant at 60 °C. Reaction time for Esterification I process was 90 minutes. The oil was purified from excess methanol and water, which was a byproduct, by heating at 130°C for 10 minutes, then cooling down. Analysis of the content of free fatty acids to see the decrease in the content of free fatty acids in low grade CPO.

2.3.2 The Esterification II Process

If the content of free fatty acids is still above 2% then the second esterification process is carried out to lower the amount of acid. The Esterification II process is a repetition of the Esterification I process, which was conducted for 60 minutes. The esterification II process is carried out to lower the acid number.

2.3.3 Transesterification

After the esterification process II is complete, the next process was the transesterification. The transesterification process is carried out when the content of free fatty acids is below 2%.

Firstly, 250 ml CPO oil is inserted into a three-neck flask equipped with a condenser and thermometer. In the three-neck round flask, methanol was mixed with molar ratio of 1: 6 with NaOH catalyst according to the variation given. methoxide solution that is a mixture between methanol and NaOH was inserted into a three-neck flask which contains CPO oil. Reaction temperature was kept constant at 60°C. The reaction time for transterification process was 60 minutes. The process of separation of methyl esters, methanol, and water was carried out using a separating funnel. Washing was done by aquades as much as 50% of the volume of oil at a temperature of 80 °C. Washing was carried out to eliminate methanol residue. Then, oil was purified from water by heating at 130°C for 10 minutes. Furthermore, the produced oil was analyzed to observe the free fatty acid content as well as the methyl esters quality.

3. RESULTS AND DISCUSSIONS

3.1. Determination of Physical and Chemical Properties of CPO

The CPO used in the study was a low grade CPO obtained from the Ministry of Industry and Trade (Disperindag) Banten Province. The results of the study of physical and chemical properties of low grade CPO samples can be seen in Table 1.

Table .1. Physical and chemical properties of off-grade CPO

Parameter	value
Water content, %	0.042
Acid value, (mg NaOH/g CPO)	49.03

Table 1 shows the content of fatty acids free of low grade CPO of 49.03%. It is higher when compared to the content of standard CPO-free fatty acids. Standard CPO has free fatty acid content of less than 5%. According to Ramadhas (2005), if the raw material used for the manufacture of biodiesel is crude oil containing high free fatty acids (i.e. more than 2%), then it is necessary to do preliminary the esterification process to lower the content of free fatty acids. A high content of free fatty acids in CPO when reacting with an alkaline catalyst (NaOH) can lead to a neutralization reaction that produces soap. The neutralization reaction mechanism is as follows:

$$\text{free fatty acids} + NaOH \rightarrow \text{Soap} + H_2O \qquad (1)$$

High water content in low grade CPO raw materials can also cause a neutralization reaction. However, the water content in low grade CPO raw materials in the study was small enough so that no preheating was needed to reduce the water content.

3.2. Effect of H_2SO_4 Catalyst Ratio on Free Fatty Acid Content

The off-grade CPO, herein as raw materials used to make biodiesel, has a high content of free fatty acids of 49.03%. So, it is necessary to conduct the esterification process previously to reduce the content of free fatty acids before transesterification process. Preliminary research was conducted to determine the effect of sulphuric acid catalyst ratio (H_2SO_4) on the reduction free fatty acid content of low grade CPO in the esterification process. The ratio of sulphuric acid catalysts used is 0.5, 1, and 1.5%. Table 2 illustrates the effect of sulphuric acid catalyst ratio on the decrease in free fatty acid content in low grade CPO.

Table 2. The effect of H_2SO_4 catalyst toward FFA content

H_2SO_4	**0.5%**	**1%**	**1.5%**
%FFA	6.41	4.59	9.91

The results showed that for variable amounts of acid catalysts used, it can be seen that the decrease in the content of free fatty acids was obtained from the esterification with amount of 1 % of H_2SO_4 catalyst. At the end of the esterification process, the maximum free fatty acid content was 4.59 %. While, the esterification using H_2SO_4 catalyst of 0.5 % and 1.5 % resulted in product with free fatty acid content 6.41 and 9.91 respectively.

The use of too few acid catalysts will result in a less maximum reaction, while the addition of too much acid catalysts is also not good because it will result in darker solution products. According to Ramadhas (2005) excess H_2SO_4 will cause a darker solution of the product, due to the formation of dimethyl esther from the reaction between excess H_2SO_4 and methanol. This will inhibit the decrease of the free fatty acids content due to the reduced amount of methanol in reaction with free fatty acids.

3.3. Percentage Reduction of Free Fatty Acids at Every Stage of the Process

The low grade CPO raw material used in the study contains 49.03 free fatty acids. So, it is necessary to do the esterification process previously to lower the content of free fatty acids before transesterification process. The esterification process uses an acid catalyst to reduce the free fatty acid content to the limit permitted for alkaline transesterification. In research that the reaction using an acid catalyst gives a very high methyl ester (Shahid et al., 2011, Ballat et al., 2010, Demirbas et al., 2008, Singh SP et al., 2010). The decrease of the content of free fatty acids at each stage of the process can be seen through Table 3.

Tabel 3. Free fatty acid content

Process stage	%FFA
CPO	49.03
Esterification I	5.643
Esterification II	0.457
Transesterification	0.111

Table 3 shows the content of free fatty acids at every stage of the process. The stages of the process are esterification I, esterification II, and transesterification. The initial free fatty acid content of low grade CPO is 49.03, then after undergoing several stages of the process the content of free fatty acids decreased to reach 0.111 in methyl ester products. The esterification reaction converts the content of free fatty acids into methyl esters and water, so that during the esterification process there is a reduction in the content of free fatty acids from low grade CPO raw materials. The esterification reaction is shon in equation 2.

$$RCOOH + CH_3OH \rightleftharpoons RCOOCH_3 + H_2O \quad (2)$$

Esterification methods are the most common way to reduce the content of free fatty acids. The advantage of reducing the content of free fatty acids by esterification method is more economical and does not produce soap, but produces methyl esters with water byproducts. The water content is very easy to remove, i.e. by heating at 130^{o}C for 10 minutes after the reaction.

The esterification reaction is carried out by two stages because the esterification I process still resulted in a large enough free fatty acid content of 5,643 %, so it can not be directly continued with the transesterification process as the content of free fatty acids is more than 2%. It is necessary to conduct esterification II process to lower the content of free fatty acids in CPO.

The esterification I process resulted in product that contain 5,643 % of free fatty acids and the esterification ii process resulted in the product with 0.457 % of free fatty acid content. There was a large decrease in free fatty acids after the esterification process II, because in esterification reaction I had a longer reaction time of 90 minutes, while for the esterification process II was only done with a reaction time of 60 minutes. The time of esterification I is longer than the reaction time of esterification II because the content of free fatty acids in cpo raw materials is still very large, so it takes a considerable reaction time. The process of esterification II of free fatty acid content in CPO is not very large anymore, so the reaction time required is not too long.

The result of the Esterification II process was the product with free fatty acids content of 0.457 %, so that the transesterification process can be done immediately. The transesterification process resulted in the biodiesel product with free fatty acids content of 0.111 5. This result already meets biodiesel quality requirements according to SNI 7182:2015 for acid number parameters.

3.4. Effect of NaOH Catalyst Ratio on Product Yield

Transesterification reaction is an alcohol reaction with triglycerides producing methyl esters and glycerol with the help of base catalysts. Commonly used base catalysts for transesterification reactions are KOH and NaOH. This refers to the journal Ballat et al., 2010 states that making biodiesel with an alkaline catalyst using sodium hydroside (NaOH) or potassium hydroside

(KOH) will produce better biodiesel. The ratio of added base catalysts is usually 0.5 - 1.5%. The catalyst used in the study was NaOH. NaOH catalyst variations added to the transesterification process vary by 0.5%; 1%; and 1.5%. The effect of NaOH catalyst ratio on biodiesel product yield can be seen in Table 4.

Tabel 4. *Yield* metil ester

NaOH	0.5%	1%	1.5%
Yield	54.8	60.8	51.2

In Table 4 indicates the yield of methyl ester from low grade CPO with NaOH catalyst ratio. The greater the yield, the more products get. Catalyst ratio of NaOH 0.5% obtained product yield 54.8%, while for catalyst ratio as much as 1% obtained product yield 60.8% and for catalyst ratio as much as 1.5% obtained product yield 51.2%. Optimum operating conditions were obtained at NaOH catalyst ratio of 1% with the largest yield yield of 60.8%.

Triglycerides contained in CPO during the transesterification process are converted into methyl esters by producing glycerol byproducts. The transesterification reaction is shown in equation 3.

$$\text{Triglycerides} + 3\ CH_3OH \rightarrow RCOOCH_3 + \text{Glycerol} \quad (3)$$

The catalyst used in the transesterification process was NaOH. The addition of too small catalyst ratios will cause a slow reaction and result in fewer product yield, while the addition of too much base catalyst ratios is also not good, as it will lead to a stockpiling reaction during the transesterification process.

3.5 Analysis of Characteristics of Methyl Ester Quality Produced

Methyl esters are then analyzed on several parameters such as free fatty acid content, density, viscosity, and water content. These parameters are then compared to biodiesel quality requirements according to SNI 7182:2015. The results of the analysis of biodiesel characteristics in the study can be seen in Table 5. Following.

Table 5. Biodiesel characteristics

No	Parameter	Experimental Results	Standar SNI-04-7182-2006
1.	Density at 40 °C, Kg/m³	870	850 -890
2.	Kinematic viscosity pada 40 °C, mm²/s (cSt)	5.381	2.3 – 6.0
3.	Water content	0.028	Maks 0.05
4.	Acid value	0.11	Maks 0.8

Biodiesel is required to have a relatively low type of weight and viscosity (viscosity) for easy flow through the injection pump. Small amounts of water in the form of dispersion in fuel are actually harmless to engine parts. For example in cold areas, they can form small ice crystals that can clog the sieve on the engine. Too high acid levels in biodiesel can cause corrosion on the cylinder walls.

Table 5 shows that the produced biodiesel in this study have met some parameters of biodiesel quality requirements according to SNI 7182:2015, so that the results obtained can be used as biodisel alternative fuels.

4. CONCLUSION

Based on the results of the research that has been done, it can be concluded: physical and chemical properties of off- grade CPO include: water content of 0.042% and free fatty acids by 49.03%. Optimum condition of esterification process is obtained with 1 % of sulfuric acid catalyst which resulted in a product with free fatty acid content of 4.59%. The process of making biodisel from off-grade CPO raw materials is previously carried out by the process of Esterification I to lower free fatty acids, followed by Esterification II, and continued with Transesterification. Product yield formed in optimum condition with NaOH catalyst ratio of 1% with product yield of 60.08%. The resulting methyl ester has a viscosity value of 5,381 Cst, density of 870 kg/m³, acid content of 0.11% and water content of 0.028%.

5. REFERENCES

Badan Pusat Statistik Indonesia., 2019, Kebutuhan bahan baku minyak mentah Import.

Balat, Mustafa, & Balat, Havva. (2010). Progress in biodiesel processing. *Applied energy, 87*(6), 1815-1835.

Demirbas, Ayhan. (2005). Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in energy and combustion science, 31*(5), 466-487.

Hayyan, A., Alam, M.Z., Kabbashi, N,A., Mirghani, M,E,S., Hakimi, N,I,N,M., Siran, Y,M., dan Tahiruddin, S., 2011, Reduction of High content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production, *Fuel Processing Technol.*, 92, 920-924.

Kattimani, VR, Venkatesha, BM, & Ananda, S. (2014). Biodiesel Production from Unrefined Rice Bran Oil through Three-Stage Transesterification. *Advances in Chemical Engineering and Science, 4*(03), 361

Maulana F., 2014. Pembuatan biodiesel dari CPO off grade dengan menggunakan reactor membrane. Skripsi Sarjana Fakultas Teknik, Universitas Riau, Pekan Baru

Ramadhas, A.S., Jayaraj, S.,Muraleedharan, C., 2005, *Biodiesel Production From High FFA Rubber Seed Oil*.

Shahid, Ejaz M., & Jamal, Younis. (2011). Production of biodiesel: A technical review. *Renewable and Sustainable Energy Reviews, 15*(9), 4732-4745

Soerawidjaja, Tatang H., 2006, *Fondasi-Fondasi Ilmiah dan Keteknikan dari Teknologi Pembuatan Biodiese,* Handout Seminar Nasional "Biodiesel Sebagai Energi Alternatif Masa Depan" UGM Yogyakarta.

Singh, S. P., & Singh, Dipti. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews, 14*(1), 200-216.

Syarfi, Nazaruddin, Zahrina I. 2010. "Pengaruh Tekanan

Transmembran Pada Pembuatan Biodiesel Dari CPO Parit Dengan Reaktor Membran". Prosiding Seminar Nasional Sains Dan Teknologi III 2010. Lampung.