

Effects of Storage Period of Waste Frying Oil to Biodiesel Conversion

Luchis Rubianto¹, Sudarminto Setyo Yuwono², Atikah³, Soemarno⁴

¹The State Polytechnic of Malang and Doctorate Program of University of Brawijaya, Indonesia

²Faculty of Agricultural Technology, The University of Brawijaya, Indonesia

³Faculty of Mathematics and Natural Science, The University of Brawijaya, Indonesia

⁴Faculty of Agriculture, The University of Brawijaya, Indonesia

Abstract

Waste frying oil is a material that potentially harmful to environment. It is also harmful to human health as suspected being a carcinogenic material. Alternatively, the oil can be used as raw material to produce renewable fuel. Storing the oil in an open container increases free fatty acids due to oxidation. Higher acids content makes more complicated in transesterification process and decreases conversion percentage. Objective of this experiment is to determine effects of storage period of waste frying oil to biodiesel conversion. The waste frying oil was originally from palm oil. In this experiment, the oil was used by two different home industries producing cassava crisps and fried bread. Each type of oil was stored in open space with period from 0 day to 90 days. The oil was converted to fatty acid methyl ester or biodiesel, a renewable fuel to replace petroleum diesel fuel, by means of alkaline process using potassium hydroxide as catalyst. Gas chromatography was used to analyze percentage of the biodiesel produced. By storing the waste frying oil to 90 days, conversion percentage decrease from 95 to 79% for waste frying oil from cassava crisps industry. Meanwhile, for the oil from fried bread industry, the figure decrease from 92 to 71%. It was found that the longer storage period the lower was the biodiesel conversion .

Keywords: Free Fatty Acid, Storage Period, Transesterification, Waste Frying Oil

INTRODUCTION

Oil fuel consumption in Indonesia always increases every year. In contrary, production of crude oil tends to decrease. According to BPS data, in 2014 the consumption is 1,3 million barrel while production is less than 0.85 million barrel per day [1].

Apart from inadequate production, oil reserve in Indonesia is only left for less than 15 years ahead. Moreover, consumption of oil for fuel is not in accordance with principles of sustainable development. Therefore, an alternative material for fuel which is more sustainable must be immediately determined [2].

In the last two decades, fuel that meets future demand must be produced from plants as part of sustainable development. At the beginning, ethanol that produced from sugarcane is expected to replace gasoline [2]. Further research on this issue is in progress to make the replacement can be put into daily practice [3].

Another research is carried out to replace diesel fuel with fatty acid methyl ester (FAME) or biodiesel that produced from plants oil or

vegetable oil. Biodiesel can be made from soybeans oil, coconut oil, palm oil, peanut oil, sunflower oil, and any oil from plants [4]. In fact, with more complicated process, it can also be produced from animal fat such as cow, sheep, goat, pig, whale, and so on.

Oil that produced from plants has a specific content. Chemically, the content composed of numbers of carbons, hydrogens, and oxygens. Structure of these atoms cause physical and chemical properties of each vegetable oil varies. One of the properties is boiling point as seen on table below.

Table 1. Properties of Oils [4]

| Plants | Contents | Boiling Point (°C) |
|-----------|-----------|--------------------|
| Palm | Palmitic | 349 |
| Coconut | Lauric | 304 |
| Corn | Stearic-1 | 371 |
| Soybean | Stearic-2 | 371 |
| Sunflower | Stearic-2 | 371 |
| Peanut | Stearic-1 | 371 |

Indonesia produces more than 10 million tones crude palm oil (CPO) annually in the last decade. In 2012, the production is more than 14

Alamat Korespondensi Penulis:

Luchis Rubianto

Email : luchis_rubianto@yahoo.com

Alamat : Teknik Kimia - Politeknik Negeri Malang

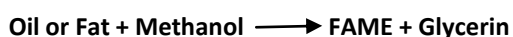
Jalan Soekarno Hatta No. 9 PO Box 04 Malang (65141)

million tones [1]. Most of the CPO is converted to frying oil. Annually, consumption of frying oil in Indonesia more than 8 million tones. That means, potential WFO as raw material to make biodiesel in Indonesia is available abundantly.

Unfortunately, production of biodiesel from CPO causes conflict of interest with foods industries and domestics consumption. Therefore, a wise decision is attempted to use waste frying oil (WFO) to produce biodiesel.

WFO comes from oil that already used for frying, already exposed to extreme heat of more than 200 °C. The heat decomposes frying oil contents, mostly as palmitate in triglyceride, to form palmitic acid as part of free fatty acid (FFA) and several chemical compounds such as aldehydes and peroxides which is suspected to cause cancer [5]. Therefore, apart from preventing harmful material entering human body, conversion of WFO to produce biodiesel causes another positive aspect. It may avoid environmental damage since WFO is potentially reducing quality of soil and water system [6].

Basically, conversion process to produce biodiesel from plant oil or WFO or animal fat known as transesterification. Chemically, they consist of a long chain of esters which generally called triglyceride. A reaction with methanol produces a shorter chain ester known as fatty acids methyl ester (FAME) or biodiesel [7]. Shorter chain means lower viscosity that can more easily be treated as liquid fuel. Generally, chemical equation of the conversion is



In fact, triglyceride is a compound that has a functional group of ester. It means the conversion is changing a type of ester to another [4][7][8]. That is why the conversion is called transesterification. In order to increase rate of reaction, a catalyst is applied. According to application of catalyst, transesterification reaction is classified into two types namely homogeneous and heterogeneous reaction. Homogeneous reaction is transesterification using liquid catalyst, such as alkaline solution. Whereas heterogeneous reaction is transesterification using solid catalyst, such as alumina, silica, and zeolite [8] [9].

Several researches show that homogeneous transesterification give a high conversion percentage but cause more complex method to separate FAME from the rest of compounds involved in the reaction. Meanwhile,

heterogeneous transesterification is less favourable in terms of conversion percentage although separation method is much easier [7].

Apart from those two types, quality of WFO is also affecting transesterification result. WFO with low FFA gives a better conversion percentage. Because FFA comes from oxidation reaction of vegetable oil, storage period of WFO prior transesterification is the main objective of this research.

RESEARCH METHOD

Experiment was the method used in this research. WFO as raw material was collected from two home industries which produce cassava crisps and fried bread located in Singosari Malang Indonesia. Both industries used fresh palm oil to fry cassava and bread for at least five times of frying and then rejected as waste frying oil. Before used for this research, WFO was filtered manually using a filter paper and cloth to separate any solid waste.

This research was mostly carried out at Chemical Engineering Laboratory of The State Polytechnic of Malang, Indonesia. It was started by dividing the already filtered WFO into nine parts. Each part was stored in an open container and labeled. Before used as raw material in a transesterification process, physical and chemical properties of the WFO, especially the colour and FFA content were analyzed in accordance with storage period.

Colour of WFO was analyzed by its absorbance using a UV-Vis Spectrophotometer. It is an instrument with double beam which has ability to measure absorbance in a range of wavelength from 200 to 800 nm. According to Lambert Beer Law, absorbance (A) is quantity of light being retained by a liquid. The darker the colour of a liquid, the higher is the value of A.

Meanwhile, the analysis of FFA content was carried out by gravimetric method. WFO from cassava and bread were analyzed separately. For each experiment, 28.2 grams of WFO was poured into a conical flask. 50 ml of hot ethanol and 2 ml of phenolphthalein as indicator were added to the flask to form a colourless mixture. The mixture was titrated with 0.1M NaOH until the mixture turned to light red solution and the colour did not change for at least 30 seconds. According to [10], FFA content then was calculated using formulae of

$$\frac{\text{ml NaOH} \times M \times \text{Molecular weight of oil} \times 100}{\text{Sample weight} \times 1000}$$

Molecular weight of oil mentioned on above formulae depends on plant as source of the oil. For examples, palm oil is mainly palmitic with molecular weight 256, coconut oil is mainly lauric with molecular weight 200 [4].

Homogeneous transesterification process was used in this research. Equipment to carry out transesterification was set up. 500 ml WFO was reacted with 100 ml methanol that was bought from local chemical store. In order to speed up the reaction, 9 grams of industrial grade of potassium hydroxide (KOH) was dissolved into the methanol prior mixing [10].

This liquid mixture was heated by means of water bath heater to 63 °C. During the heating, the temperature was maintained just below the boiling point of methanol (65 °C). Furthermore, to avoid methanol vapour escaping, a reflux equipment was added. The process was allowed to progress for 30 minutes.

After heating, the mixture was allowed to cool naturally. The mixture became produce two layers with lower layer darker than the upper one. The darker layer was by product known as glycerin or glycerol. Glycerin is a compound that dissolves in water. It has an economic value because it can be used as raw material for several industries such as cosmetics, explosives, and plastics. Later, by product was decanted by means of a separating funnel [10]. The clear liquid left in the funnel was the main product, FAME or biodiesel. The product was washed by pouring 50 ml hot water two times in order removes any left glycerin, since glycerin is soluble in water while FAME is not.



Figure 1. Separation of FAME – Glycerin using funnels

The product was washed by pouring 50 ml hot water two times in order remove any left glycerin, since glycerin is soluble in water while FAME is not. After separation, the experiment was continued with analysis of physical properties of FAME which related with fuel. The properties were density, viscosity, and flash point.

Density of FAME was analyzed using KEM Kyoto Electronic DA-100. An amount of FAME was inserted to input tube. Its density then was showed digitally.

Viscosity of FAME was analyzed using KOEHLER CFR 200 and CFR 350 that met standard of ASTM D446. An amount of FAME was poured on top of the equipment then allowed to flow downward. By recording the time required by FAME to flow from top mark to bottom mark, its viscosity was calculated.

Meanwhile, flash point of FAME was analyzed using KOEHLER K-16270. 50 ml of FAME was put in the provided cup. It was then electrically heated with moderate heating. Simultaneously, a pilot flame as ignition source. Periodically, the flame was turn into the cup. As the vapour of FAME formed during heating, it was accumulated on top of the cup. When the accumulation was sufficient, the vapour ignited vigorously and cause the flame extinguished.

Separately, the product was also analyzed using a gas chromatography (GC) [11]. Gas chromatography is a method to separate a mixture into its components which must be two or more compounds. The separation occurred due to the difference of boiling point of each compound and interaction of two phases, namely mobile phase and stationary phase [12].

Mobile phase was components moving along the column. The movement was caused by pure pressurized gas such as nitrogen. This gas flowed at particular flow rate to carry injected sample moved along the column through a detector.

Stationary phase was particles inside the column. These particles were layered with chemicals which have a particular polarity. This large surface area controlling the movement of each sample molecule hence its retention time [12].

In this research, gas chromatography was used to ensure that the main product was FAME. The gas chromatography instrument was made by Hewlett Packard with FID (flame ionization detector) and OV1 semi polar column. Flow rate of carrier gas (pure nitrogen, N₂) was set at 30

ml/minute and column temperature was set at 200 °C [10].

First, pure FAME from Pertamina as standard was diluted with methanol to make 50% solution. An amount of benzyl alcohol as external standard was also added to guarantee consistency of quantitative analysis. 2 µl of the solution then was injected to gas chromatography. A chromatogram was printed and carefully analyzed.

Second, the FAME produced from the experiment was treated exactly the same as the first one. It was then injected to the chromatography. Its chromatogram then was also analyzed and compared to the first one.

RESULTS AND DISCUSSION

Visually, the colour of WFO from fried bread is darker than that of cassava crisps. Data from UV-Vis Spectrophotometer is shown as follow.

Table 2. Data from UV-Vis Spectrophotometer

| No | Storage Period (Days) | Absorbance | |
|----|-----------------------|------------|-------|
| | | Crisps | Bread |
| 1 | 0 | 0.265 | 0.623 |
| 2 | 1 | 0.265 | 0.624 |
| 3 | 2 | 0.265 | 0.624 |
| 4 | 3 | 0.265 | 0.624 |
| 5 | 7 | 0.268 | 0.629 |
| 6 | 15 | 0.272 | 0.647 |
| 7 | 30 | 0.288 | 0.683 |
| 8 | 60 | 0.314 | 0.701 |
| 9 | 90 | 0.385 | 0.738 |

Data on that table shows that the longer storage period, both WFO from crisps and bread become darker due to oxidation process. Oxidation also reducing transesterification percentage that will be determined by gas chromatography analysis. One of chromatogram shown on figure 3, the result of transesterification of WFO from crisps with storage period 0 days.

Another interesting result is also determined on this research. FFA contents of WFO from crisps are slightly lower than those of bread. The fact is the colour of WFO from cassava crisps is light brown while from bread is much darker. Data from gravimetric analysis show that FFA contents as on below table.

Table 3. Free Fatty Acids Content in WFO

| No | Storage Period (Days) | FFA (%) | |
|----|-----------------------|---------|-------|
| | | Crisps | Bread |
| 1 | 0 | 0.23 | 0.29 |
| 2 | 1 | 0.43 | 0.48 |
| 3 | 2 | 0.85 | 0.91 |
| 4 | 3 | 1.30 | 1.38 |
| 5 | 7 | 2.20 | 2.31 |
| 6 | 15 | 3.50 | 3.72 |
| 7 | 30 | 4.89 | 5.04 |
| 8 | 60 | 5.32 | 5.83 |
| 9 | 90 | 5.68 | 6.02 |

Transesterification process to both types of WFO that stored less than 30 days was carried out without problem. However, with FFA content more than 5%, two layers that usually formed during transesterification did not appear. The layers were not clearly separated. They formed a bulky mixture. Apparently, soap appeared during the reaction to form emulsion [13].

Previous experiment using waste frying oil that originally from soybeans oil showed that formation of soap, also known by saponification, was a result of reaction of triglyceride and alkaline [8]. Using waste frying oil that originally from canola oil [14] and from sunflower seeds oil [15] also showed similar result. Because the FFA content is high (more than 5%), some of the potassium hydroxide, that intentionally used as catalyst, reacts with the FFA and become neutral. Saponification is then occurred as the rest of potassium hydroxide reacts with triglyceride. The effect of saponification was reduced by allowing the mixture to rest at least for 24 hours. Afterwards, the two layers formed as usual.

Saponification is a common problem in homogeneous transesterification. This will not be the case in heterogeneous one [16][17]. Beside saponification, another unwanted matter in high FFA content is unpleasant odour. Usually, a pungent odour indicates that FFA content in vegetable oil, including WFO, is high [18][19].

In this experiment, storing waste frying oil that originally from palm oil changed physical properties of FAME or biodiesel produced. The properties data of FAME were determined and recorded as on following table.

Table 4. Physical Properties of FAME

| Storage Period of WFO (Days) | Density (kg/ltr) | Viscosity (cSt) | Flash Point (°C) |
|------------------------------|------------------|-----------------|------------------|
| 0 | 0.87 | 4.9 | 82 |
| 1 | 0.87 | 4.9 | 82 |
| 2 | 0.87 | 4.9 | 84 |
| 3 | 0.87 | 5.2 | 84 |
| 7 | 0.87 | 5.2 | 86 |
| 15 | 0.88 | 5.4 | 86 |
| 30 | 0.88 | 5.7 | 86 |
| 60 | 0.88 | 5.9 | 88 |
| 90 | 0.88 | 6.2 | 88 |

Most of above data resemble with data from Pertamina. Specifications of diesel fuel are: density 0.82-0.85 kg/ltr, viscosity 2.0-4.5 cSt, and flash point minimum 55 °C. Viscosity is the only physical property that does not meet fuel specification.

Gas chromatography analysis method creates a chromatogram. The chromatogram of FAME that produced from WFO stored in 0 day is shown on following table.

Table 5. Chromatogram of FAME

| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] |
|--------|------------|---------------|-------------|----------|
| 1 | 1.566 | 10494965.49 | 654023.92 | 59.13 |
| 2 | 5.615 | 2732.09 | 120.39 | 0.02 |
| 3 | 6.180 | 8417.44 | 310.96 | 0.05 |
| 4 | 7.910 | 81261.82 | 2969.03 | 0.46 |
| 5 | 9.291 | 3070481.91 | 116437.73 | 17.30 |
| 6 | 10.403 | 3990719.90 | 143045.38 | 22.49 |
| 7 | 11.528 | 88960.89 | 2536.19 | 0.50 |
| 8 | 12.648 | 2864.72 | 106.91 | 0.02 |
| 9 | 13.653 | 7332.09 | 228.19 | 0.04 |
| | | 17747736.35 | 919778.70 | 100.00 |

Missing Component Report
 Component Expected Retention (Calibration File)

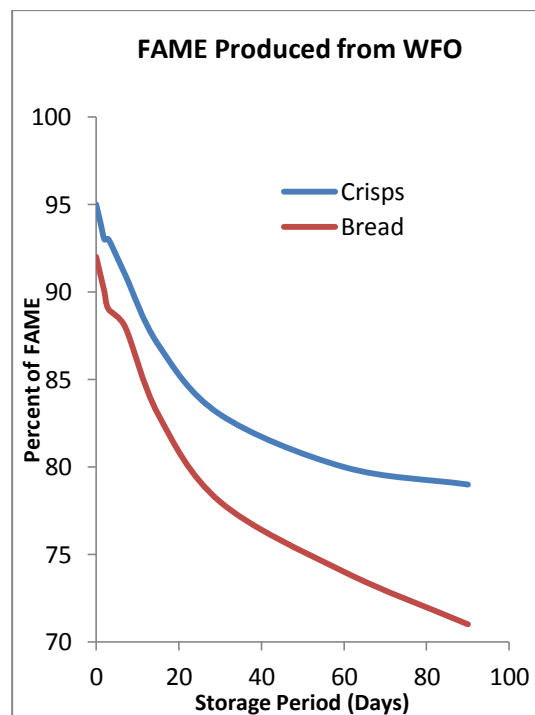
All components were found

The first column of the table shows the number of the peak. There are 9 peaks detected meaning 9 different compounds in the FAME. The first peak indicates methanol that added as solvent to dilute sample in GC analysis. The second column is retention time (Rt) that gives information of type of compound for qualitative analysis. Under the same operation conditions of

GC analysis, the same compound always has identical Rt. Apart from retention time, the chromatogram also provides data for quantitative analysis. Quantity of FAME can be seen from area percentage (Area [%]), the last column.

On the chromatogram, there are three main peaks. The first peak with retention time 1.57 minutes indicates methanol that used to dilute sample before injected to the GC. The second peak with retention time 9.29 minutes indicates the presence of benzyl alcohol as external standard. The third peak with retention time of 10.40 minutes is the peak of FAME. Several small peaks also present indicating impurities.

Retention time is a period that required by a compound to travel from injection port to detector passing length of a column. The period is highly depends on flow rate of carrier gas, temperature of the column, and boiling point of the compound. Under the same conditions (gas flow rate and column temperature), the lower the boiling point of a compound, the smaller is the retention time [12]. Besides that, the same compound usually has the same retention time despite the compound is in its pure form or in a mixture. Pure FAME has a retention time of 10.40 minutes.



Graph 1. FAME Produced from Stored WFO

Amount of FAME that has retention data of 10.403 minutes is 22.49%. It should be bear in mind that this mixture contains three distinctive compounds, namely: FAME, benzyl alcohol, and methanol. On the chromatogram, retention time of methanol is 1.57 minutes with quantity 59.13%. Reducing quantity of methanol and benzyl alcohol in the mixture, content of FAME is calculated as $22.49/(100 - 59.13 - 17.30)$. The result is 95% which is the highest conversion in this research.

By processing chromatograms data, the result can be concluded on the graph below.

CONCLUSIONS

Storage period of WFO affecting the conversion of biodiesel production. The longer period of WFO storage makes its FFA content increase. Consequently, high FFA content cause transesterification less effective therefore biodiesel percentage decrease. By storing WFO up to 90 days, the conversion of WFO to produce FAME decreasing by almost 25%. Recommendation as outcome of this research is immediately carry out WFO processing in order to maximize the conversion of biodiesel production.

ACKNOWLEDGEMENT

Appreciations must be addressed to technicians, especially Mr. Kaliawan and Mr. Zulriadi who have been assisting along the experiments at Laboratory of Chemical Engineering of The State Polytechnic of Malang.

REFERENCE

- [1]. Badan Pusat Statistik (BPS) Republik Indonesia. 2014. Data Strategis 2013.
- [2]. Beer T, Grant T, Brown R, Edwards J, Nelson P, Watson H, Williams D. 2000. Life-cycle Emissions Analysis of Alternative Fuels for Heavy Vehicles. CSIRO Atmospheric Research Report. C/0411/1.1/F2
- [3]. Howe CW. 1979. Natural Resource Economics: Issue, Analysis, and Policy. John Wiley & Son Pub. New York, USA
- [4]. Ng JH, Hoon Kiat Ng, Suyin Gan. 2010. Advances in Biodiesel Fuel for Application in Compression Ignition Engines. *Clean Tech Environ Policy*. 12: 459-493
- [5]. Krivoshto IN, Richard JR, Albertson TE, Derlet RW. 2008. The Toxicity of Diesel Exhaust: Implications for Primary Care. *Journal American Board Family Medicine*. 21: 55-62
- [6]. Lapinskiene A, Martinkus P, Rebzdaite V. 2006. Eco-toxicological Studies of Diesel and Biodiesel Fuels in Aerated Soil. *Environmental Pollution*. 142: 432-437
- [7]. Asakuma Y, Maeda K, Kuramochi H, Fukui K. 2009. Theoretical study of the transesterification of triglycerides to biodiesel fuel. *Fuel*. 88: 786-791
- [8]. Bautista LF, Vicente G, Rosalía Rodriguez R, Pacheco M. 2009. Optimisation of FAME Production from Waste Cooking Oil for Biodiesel Use. *Biomass and Bioenergy* . XXX: 1-11
- [9]. Baiju B, Naik MK, Das LM. 2009. A Comparative Evaluation of Compression Ignition Engine Characteristics using Methyl and Ethyl Esters of Karanja Oil. *Renewable Energy* 34: 1616-1621
- [10]. Rubianto L., Sudarminto, Atikah, Soemarno. 2013. Waste Frying Oil as Source of Alternative Energy. *Research Inveny: International Journal Of Engineering And Science*. Vol.2. Issue 8: 28-32
- [11]. Rubianto L., Sudarminto SY, Atikah, Soemarno. 2013. Comparison of Biodiesel and Petrodiesel Particulate Emission. *The International Journal Of Engineering And Science (IJES)* Vol. 2. Issue 5: 66-69
- [12]. Engewald W, Dettmer-Wilde K. 2014. *Practical Gas Chromatography*. Springer Verlag Berlin Heidelberg. Germany
- [13]. Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In S. 2009. A Comparative Study of KOH/Al₂O₃ and KOH/NaY Catalysts for Biodiesel Production via Transesterification from Palm Oil. *Renewable Energy*. 34: 1145-1150
- [14]. Chhetri AB, Watts KC, Islam MR. 2008. Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production. *Energies*. 13-18
- [15]. Demirbas A. 2009. Biodiesel from Waste Cooking Oil via Base-catalytic and Supercritical Methanol Transesterification. *Energy Conversion and Management* 50: 923-927
- [16]. Chen YM, Xiao B, Chang J, Fu Y, Pengmei Lv, Wang X. 2009. Synthesis of Biodiesel from Waste Cooking Oil using Immobilized Lipase in Fixed Bed Reactor. *Energy Conversion and Management*. 50: 668-673

- [17]. Dizge N, Aydiner C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B. 2009. Biodiesel Production from Sunflower, Soybean, and Waste Cooking Oils by Transesterification using Lipase Immobilized onto a Novel Microporous Polymer. *Bioresource Technology*. 100: 1983–1991
- [18]. Kaul S, Porwal J, Garg MO. 2010. Parametric Study of Jatropha Seeds for Biodiesel Production by Reactive Extraction. *J Am Oil Chem Soc*. 87: 903–908
- [19]. Myint LL, El-Halwagi MM. 2009. Process Analysis and Optimization of Biodiesel Production from Soybean Oil. *Clean Technology Environ Policy*. 11: 263–276