Effect of transesterification on the result of waste cooking oil conversion to biodiesel

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Abstract. Biodiesel is one of the greenest alternative fuels and can be produced from vegetable, waste cooking, and animal oils. Waste cooking oil is one of the raw materials that have a high chance of making biodiesel because it contains a very abundant triglycerides. It is reacted with alcohol and NaOH catalyst through a transesterification reaction. Transesterification takes place inside a three-neck flask that has been equipped with condenser reflux, magnetic stirrer, and a thermometer. To know the effect by using variations of 60 minutes, 90 minutes, 120 minutes, and 150 minutes In this study, the optimum biodiesel conversion of WCO catfish seller was 85.2% preselected at a 1:6 molar ratio, with 1% NaOH catalyst in 60 minutes. Meanwhile, conversion biodiesel from WCO of household used and WCO of fried sellers were respectively 82.34% and 82.20%. Based on the test of biodiesel properties resulting from the density, viscosity, acid number, water content, flash point and PH that biodiesel have been compliant with SNI. Biodiesel density of 880 kg/m³, acid number 0.27 mg-KOH/g, and has a maximum water content of 0.05. This biodiesel has the main compound the name is palmitic acid which 45.73%.

1. Introduction

Energy is one of the most important needs of human life. Most of the energy is still needs to be supplied from non-renewable natural resources such as petroleum, natural gas, and coal which will sooner or later be depleted [1-3]. The advanced research and use of diesel motors in the industry are unlikely to stop just because of the depletion of fossil fuels. Biodiesel is an alternative fuel made from renewable natural resources [4]. Potential oils can be used as raw material for making biodiesel, namely waste cooking oil (WCO) vegetable oil, jatropha oil, and animal oil. WCO include hazardous waste because they contain carcinogenic substances that will pollute the soil and water when expelled. Therefore, it is necessary to use the waste of WCO [3]. WCO has potential as a raw material for making biodiesel because it has a lot of triglycerides and has not been utilized optimally [5-7]. However, the viscosity of waste cooking oil needs to be lowered so as not to inhibit the injection process on diesel engines. One of the reactions that can decrease the viscosity of cooking oil is the transesterification reaction that produces methyl esters. According to the results of research that has been done from 2005 to present shows that biodiesel produced from WCO has a quality equivalent to biodiesel according to ASTM standards, so that biodiesel from the conversion of cooking oil has a chance to be marketed both domestically and for exported [1].
This biodiesel is produced through a transesterification process [7-9]. This process begins with the analysis of raw materials or acid test to obtain free fatty acid or Free Fatty Acid (FFA). In the transesterification process, methanol and oil are reacted with alkali hydroxide as an alkaline catalyst to speed up the reaction rate. The main products resulting from this reaction are methyl esters or biodiesel and produce a by-product of glycerol. Transesterification reactions are influenced by several important factors such as catalysts, the molar ratio of oils with alcohols, as well as reaction time of heating. Previous research says transesterification using a homogeneous catalyst of Sodium Hydroxide or NaOH with the raw material of vegetable oil can be completed in a short time that is 1 hour of reaction [3]. The magnitude of the conversion value of biodiesel is also influenced by the amount of molar oil and methanol used. The larger biodiesel conversion indicates the optimum condition of the biodiesel. The condition of the type of waste cooking oil obtained from different sources will result in different biodiesel optimum conditions. There are several factors that affect the condition of each different WCO such as used in frying, multiple uses in frying, and the level of impurities contained in WCO. However, no research has been done to determine the optimum condition of biodiesel with raw materials of WCO obtained from different sources. This final project research has a purpose to get the conversion of biodiesel produced based on the influence of reaction time with a variation of molar ratio and amount of catalyst, and to know the optimum condition of biodiesel produced from three different types of WCO source. And obtain the result of biodiesel characteristic based on SNI [10].

2. Basic Theory and Research Methodology

2.1 Waste Cooking Oil

Waste cooking oil is a waste that comes from households, restaurants and food industries. Waste oil produced during the heating process (frying) over some time contains some harmful compounds (carcinogenic) such as free radicals that can grow cancer cells in the human body. Besides, physical changes that occur during heating cause changes in refractive index, viscosity, the color becomes brownish/blackish, smell and decrease of fuel point [3]. Due to the complex reaction of the oil, the unsaturated fatty acid bond turns saturated. The higher content of saturated fatty acids in oil signifies the decreasing quality of the oil [4]. Table 1 shows the content data of cooking oil.

| Parameter                  | Content     |
|----------------------------|-------------|
| Density (kg/m³)            | 910.4       |
| Kinematic viscosity 40°C   | 39.07       |
| Acid number                | 1.0037      |
| Water content, % volume    | 1.24        |
| Peroxide number, mg        |             |
| O2/100g                    | 0.0168      |
| Flash point (°C)           | 247.7       |

Table 1. Data content of WCO [1]

Waste cooking oil as raw material for biodiesel production can be grouped into two types based on FFA content [5] as follow:

a. Vegetable oil with FFA content less than 2%, transesterification process can be done,
b. Vegetable oil with FFA content of more than 2%, the esterification process first then followed by the transesterification process.

2.2 Transesterification

Transesterification is a process that reacts triglycerides in cooking oil with methanol to produce fatty acid methyl esters (FAME) or biodiesel and glycerol as byproducts. Some of the things that affect the transesterification reaction are:
a. The influence of water content in WCO. Cooking oil to be transesterified must be water-free because water will react with the catalyst so that the amount of catalyst will be reduced. The catalyst must be avoided from contact with air to avoid reaction with water vapor and carbon dioxide. Also, the cooking oil to be transesterified should have a free fatty acid number less than 2%.

b. Comparison of molar oil and methanol. More the amount of alcohol used then the resulting methyl ester conversion will increase. According to some studies, the best molar ratio is 1:9 because it can produce optimum yield. The yield of biodiesel will decrease when the molar ratio of oil to methanol is more than 1: 9. This is because methanol can act as an emulsion in the reaction mixture [6].

c. Amount of catalysts. The catalyst function to accelerate the reaction and decrease the activation energy so that the reaction can take place at room temperature. Previous research says, without catalyst reaction will last long enough and can take place at a temperature of 250°C. The catalysts commonly used in transesterification reactions are base catalysts such as potassium hydroxide (KOH) and sodium hydroxide (NaOH).

d. Reaction time. The reaction time may affect the biodiesel produced from the transesterification process. For the chemical reaction is known that the longer reaction time, the interaction between molecules is more intensive and produce more products.

2.3 Research Methodology
2.3.1 Transesterification Process

The experiment was conducted by an experimental method with one step reaction, i.e. transesterification reaction. The raw materials used are WCO and methanol with base catalyst sodium hydroxide (NaOH). The changed variable used is the molar ratio of oil with methanol of 1: 3, 1: 6, 1: 9, 1:12 and 1:15, the amount of catalyst as much as 0.75% and 1%, and the variation of reaction time taken in the transesterification reaction 60 minutes, 90 minutes, 120 minutes and 150 minutes. Table 2 is the determination of the number of biodiesel samples to be made based on variations of variables. The variable used by one of the samples showing the optimum biodiesel conversion is called the optimum variable. The optimum variable will be used in the synthesis of biodiesel with the type of WCO obtained from other sources. Then, there will be the difference of biodiesel conversion produced from three types of raw materials of WCO.

| Ratio Mol | 1:3 | 1:6 | 1:9 | 1:12 | 1:15 |
|-----------|-----|-----|-----|------|------|
| 0.75%     |     |     |     |      |      |
| 1%        |     |     |     |      |      |
| T         | S1  | S5  | S9  | S13  | S17  |
| i         | S2  | S6  | S10 | S14  | S18  |
| m         | S3  | S7  | S11 | S15  | S19  |
| e         | S4  | S8  | S12 | S16  | S20  |
|           |     |     |     |      |      |
| S1 = Sample 1 made using a molar ratio of oil and methanol 1: 3 and catalyst 0.75% |
| S9 = Sample 9 made using a molar ratio of oil and methanol 1: 9 and catalyst 0.75% |

Before the transesterification process, the process of purification of crude oil should be done first. The refining of WCO is the separation of the degradation reaction product from the oil. To remove the dense impurities that settle on the WCO, filtering process using filter paper done. The transesterification process is carried out in a three-neck flask with condenser reflux, magnetic stirrer, and thermometer. The series of equipment can be seen in Figure 1.
This research uses 100 grams of cooking oil that has been mixed with methanol and catalysts in determined amounts. The transesterification reaction is carried out at 60 °C. The product formed is then deposited to obtain two layers, the top layer is biodiesel, and the bottom layer is glycerol. Furthermore, a separation between biodiesel and glycerol was performed. The transesterified biodiesel then washed using warm water many times until PH product from each sample is neutral. The washing process also aims to remove alcohol and unreacted catalysts. The biodiesel is then fed into the oven at a temperature of 100°C for 2 hours to remove the remaining water content until be produced a pure product then result of conversion and analyze of density, viscosity, flash point, and fatty acid content. Along with Gas Chromatography-mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) laboratory.

2.3.2 Analyze the results of the transesterification process
After the transesterification process and produced pure biodiesel, it is necessary to calculate the conversion of biodiesel from each sample. The purpose of conversion calculation is to determine the optimum condition of biodiesel produced [7].

\[
\text{Conversion (\%)} = (1 - \frac{AV_{OL}}{AV_{WCO}}) \times 100
\]

with AV OL (Acid Value of Oil Layer) = acid number of crude biodiesel after separated from the glycerol layer in the transesterification process, and AV WCO (Acid Value of Waste Cooking Oil) = an acid number from the raw material of WCO.

2.3.3 Analyze the result of FTIR
FTIR laboratory tests can identify the material and presence of existing functional groups, to detect the presence or absence of other mixtures in a material by functional group analysis of the material. The working principle of FTIR spectroscopy is the interaction of energy with matter. The interaction of matter form of molecules complex compounds with infrared energy causes molecules to vibrate where the magnitude vibrational energy of each component of the molecule varies depending on the atoms and the bonding strength that connects them to different frequencies.

2.3.4 Analyze the result of GCMS
The instrument of this tool is a combination of GC and MS tools; this means that samples to be checked are identified first with GC (Gas Chromatography), then identified with MS (Mass Spectrometry) tool. GC and MS are simultaneous combination forces to separate and identify mixed components. GCMS can only detect volatile compounds. When the compound is inserted in mass spectroscopy, the compound will be collision by the electron, and the molecule will experience a fragmentation reaction. The molecule will break apart by the collision of electrons in the spectrometer. The outbreak of the
molecule depends on the functional group present in the molecule. In the presence of fragmentation can recognize the compound whether including the class of alcohol, carboxylate, aldehydes, and so forth.

3. Results and Discussion

3.1 Analyze of raw materials

Free fatty acids or FFA is the degradation of triglycerides, as a result of oil damage due to repeated use. The higher FFA, then the higher level of oil damage. In transesterification process for biodiesel production, FFA value >2% will cause saponification on biodiesel; then the esterification process is done first. Based on Table 3, raw materials obtained from catfish sellers, households and fried sellers have free fatty acid or FFA respectively are 1.3394%, 0.8754%, 1.0049%. It shows that the transesterification process can be done with base catalyst without esterification process in making biodiesel.

| Source of raw material | Acid number | FFA (%) | Density (kg/m³) | Viscosity (cSt) | Water content (%) |
|------------------------|-------------|---------|-----------------|----------------|------------------|
| Catfish restaurant     | 1.8346      | 1.3394  | 924.1           | 64.41          | 1.328            |
| Household used         | 0.8222      | 0.8754  | 980.1           | 60.96          | 1.415            |
| Seller of fried        | 1.1011      | 1.0049  | 965.1           | 50.36          | 1.476            |

The transesterification process is carried out by mixing the cooking oil, methanol and the base catalyst NaOH with a certain amount according to the variable. Variations of variables used in the process of transesterification using WCO from catfish seller are molar ratio and catalyst. In the next subsection will be explained about the influence of reaction time based on these variables. The transesterification process will produce two products, namely biodiesel and glycerol as by-products. The presence of glycerol as a by-product shows that biodiesel synthesis is successful. Next is the separation between glycerol and biodiesel, washing with water, until the drying process.

3.2 Effect of reaction time to biodiesel conversion

![Figure 2. Conversion relation to reaction time based on molar ratio variation with amount of: (a) NaOH Catalyst 0.75%, (b) NaOH Catalyst 1%](image)

Making this biodiesel is done in temperature 60 °C and kept the temperature stable. This because the reaction temperature of 60 °C is the optimal temperature to produce optimal conversion [8]. Based on Figure 2a, at 60 minutes conversion was obtained at 84.87% at a 1: 6 molar ratio and a conversion of 55.60% was obtained at a 1:12 molar ratio. While at 90 minutes showed that the conversion results decreased in several molar ratios such as 1: 6 and 1: 9, ie, 74.90% and 75.18%. The subsequent addition of time leads to stable conversions within 90-150 minutes at a 1: 3, 1: 6 and 1: 9 molar ratio. This is
because the optimum reaction has been achieved within 60 minutes. The reaction occurring in the transesterification process is reversible when the optimum conversion has been achieved, the reaction will minimize the product obtained [9]. Figure 2b shows that on the use of 1% NaOH catalyst in 60 minutes reaction time the highest conversion was obtained at 85.26% at a 1: 6 molar ratio, and conversion of 69.94% at a 1:12 molar ratio. With the same reaction time obtained a biodiesel conversion of 80% in 1: 9 and 1:15 molar ratio. Within 90 minutes to 150 minutes shows stable conversion results in 1: 3, 1: 6, 1:12 and 1:15 molar ratios. This is because the optimum reaction has been reached within 60 minutes, then the addition of time will not increase the conversion. The longer the reaction time, the greater the possibility of contact between substances resulting in a large conversion. But if equilibrium is reached, then with increasing reaction time will not increase the conversion result [9]. From the above, each using a catalyst of 0.75% and 1%, obtained results that in a molar ratio of 1: 6 and 60 minutes reaction time can result in optimum biodiesel conversion of 84.87% and 85.26%.

3.3 Effect of Optimum Reaction Time on Conversion Based on Catalyst Variation

In addition to the molar ratio, the amount of catalyst also greatly influences the conversion of biodiesel. In previous experiments, the use of 0.75% catalyst can result in a 90% biodiesel conversion [10]. The purpose of adding 1% catalyst variation is to compare the conversion of biodiesel conversion obtained. Figure 4 is obtained from the transesterification process using WCO of catfish seller at a molar ratio of 1: 6 and within 60 minutes of reaction time, it is seen that the conversion increases in the use of 1% catalyst amount. The greater some catalysts resulting reaction conversion is also higher. In other experiments, the use of 12% catalyst amounts can result in up to 93.2% conversion [11] But the lack of use an increasing number of catalysts, make saponification in the result of biodiesel, so make a difficult separation between glycerol, and biodiesel.

![Conversion Relation to Optimum Reaction Time at Molar Ratio of 1: 6 with Variation Amount of NaOH Catalyst 0.75% and 1%](image)

**Figure 3.** Conversion Relation to Optimum Reaction Time at Molar Ratio of 1: 6 with Variation Amount of NaOH Catalyst 0.75% and 1%

Figures 2a and 2b in the 1: 6 molar ratio show that in reaction time of 90 minutes to 150 minutes the conversion looks stable. It shows that at this time susceptible the catalyst has reached a saturation point after doing the high activity at reaction time 60 minutes. The relation of reaction time to optimum conversion was achieved at 60 minutes with 1% catalyst amounting 85.26%. The optimum variables are 1: 6 molar ratio, 1% NaOH catalyst and 60 minutes reaction time. The optimum variable will be used in the synthesis of biodiesel with WCO from households used and fried sellers.
3.4 Analysis of Biodiesel Results Using Fourier Transform Infra-Red (FTIR)

Analysis of biodiesel results with an FT-IR spectrophotometer was performed to prove the presence of ester in the transesterification product as well as to determine the difference between spectra produced from WCO and biodiesel. The presence of esters can be seen from typical uptake of C = O and C-O groups. The results are identified with FT-IR spectrophotometer can be seen in Figure 4. The blue spectrum line is the result of biodiesel, while the yellow spectrum is the result of WCO. From the results obtained that the visible spectrum between WCO with biodiesel is not much different. This difference identifies that the transesterification reaction has taken place by showing that there is an ester compound which is a compound of biodiesel [10]. For regions division, regions one with the range of 4000 to 2500, region two has a range of 2500 to 2000, the third region ranges from 2000 to 1500, and the four region range from 1500 to 500. The result of the FTIR analysis of cooking oil can be seen in Figure 5.

![Figure 4. FTIR analysis of WCO and biodiesel](image)

| Area(cm⁻¹) | Wave number | Characteristic Cluster       |
|------------|-------------|------------------------------|
| WCO        | Biodiesel   |                              |
| 3500-3300  | 3331.07     | Absorption OH                |
| 2850-2750  | 2735.06     | Absorption C-H               |
| 1300 - 1000| 1170.79     | C-O uptake indicating the presence of an ester |

In analyzing the IR spectra, a review of the major functional groups of biodiesel constituents, such as hydroxyl groups (O-H), and C-H uptake in organic compounds. OH uptake is present in an area of 3500-3300 cm⁻¹. Esther gave rise to strong and strong C-O uptake at 1300-1000 cm⁻¹. While C-H has a weak and sharp intensity at 2850-2750 cm⁻¹[11], the biodiesel spectrum analysis of WCO household and raw materials containing cluster characteristics based on wave values are presented in Table 4.

3.5 Analysis of Biodiesel Results Using Gas Chromatography-Mass Spectrometry (GC-MS)

Analyzes with GC-MS were used to determine the type of compounds contained in methyl esters from WCO. This analysis yields spectra peaks which each show a specific type of methyl ester. The result of GC-MS analysis is shown in Figure 5. A compound is said to be similar to a standard compound if it has the same molecular weight, similar fragment patterns, and SI values (similarity index) are high.
Figure 5. Results of GC-MS Analysis

The main compounds that are the major components from compounds contained in the biodiesel are seen from the magnitude percentage of the compound. Other compounds resulting from analysis by Gas Chromatography, possibly an alkyl ester derivative from each fatty acids.

3.6 Biodiesel Characteristics Generated By Three Sources of Raw Materials

| Characteristic   | Oil Name          | Acid number | Density (kg/m³) | Viscosity (cSt) | Water content | PH |
|------------------|-------------------|-------------|-----------------|-----------------|---------------|----|
|                  | Catfish restaurant| 0.2704      | 880             | 5.18            | 0.03          | 7  |
|                  | Household used    | 0.2769      | 880             | 4.95            | 0.05          | 7  |
|                  | Seller of fried   | 0.2775      | 880             | 4.47            | 0.01          | 7  |
|                  | SNI Standard      | Maks. 0.8   | 850 - 890       | 2.3 – 6.0       | Maks. 0.05    | 7 - 8 |

Based on Table 5, the biodiesel produced by the three types of WCO obtained from different sources in the synthesis process using the amount of 1% NaOH catalyst, the molar ratio of oil and methanol 1:6, and in reaction time of 60 minutes. The three biodiesels have water content respectively are 0.03, 0.05 and 0.01, and have a neutral acid pH is 7. The biodiesel also has an acid number of 0.27, a density of 880 kg/m³, and a viscosity below 6.0 cSt. In this experiment, it can be concluded that the biodiesel produced is following SNI 04-7182-2006 standard.

4. Conclusion

Based on above discussion, we can conclude:

a. Optimum variables obtained are a molar ratio of oil and methanol of 1:6, some catalyst NaOH 1% and reaction time 60 minutes.

b. Conversion of biodiesel produced from three kinds WCO obtained from different sources include catfish seller of 85.26%, household used of 82.34%, and 82.20% are fried sellers.

c. Characteristics of biodiesel produced from the three kinds of WCO have fulfilled the SNI standards which include density, viscosity, acid number, moisture content, and PH.

References
[1] Cuadri A A, García-Morales M, Navarro F J and Partal P 2014 Chem Eng Sci 111 126
[2] Kawentar W A and Budiman E 2013 Energy Procedia 32 190
[3] Freedman B, Pryde E H and Mounts T L 1984 J Am Oil Chem Soc 61 1638
[4] Putrasari Y, Nur A and Muharam A 2013 Energy Procedia 32 21
[5] Supple B, Howard-Hildige R, Gonzalez-Gomez E and Leahy J J 2002 *J Am Oil Chem Soc* **79** 175
[6] Enweremadu C C and Mbarawa M M 2009 *Renew Sustain Energy Rev* **13** 2205
[7] Wong Y, Ou S, Liu P, Xue F and Tang S 2006 *J Mol Ch A: Chem* **252** 107
[8] Lam M K, Lee K T and Mohamed A R 2010 *Biotechnol Adv* **28** 500
[9] Phan A N and Phan TM 2008 *Fuel* **87** 3490
[10] Badan Standarisasi Nasional. 2006. Standar Nasional Indonesia: Biodiesel. Nomor 04-7182-2006 (Jakarta: National Standardization Board of Indonesia)
[11] Zhang Y, Dude M A, McLean D D and Kates M 2003 *Bioresource Technol* **89** 1