Synthesis Biodiesel from Waste Cooking Oil with Microwave Irradiation Method as Alternative Renewable Energy Source

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Abstract. Biodiesel is a very potential fuel to replace diesel fuel. WCO can be used as raw material for making biodiesel. One method of making biodiesel is by using microwave irradiation. Microwave heating is more advantageous than conventional method heating, because conventional method heating is very slow and inefficient. This study aims to determine the effect of power, reaction time and physical properties of raw materials in the manufacture of biodiesel from waste cooking oil using microwave irradiation. The experimental stage consists of pretreatment, transesterification, separation, washing, and analysis of biodiesel yields. Transesterification of waste cooking oil takes place in a microwave oven by: (a) variations in microwave power (100, 180, 300, 450, and 600 Watt) at 5 min, and (b) reaction time variation (5, 10, 15, 20 and 25 minutes) at a fixed power of 100 Watt. From the research it is known that the operating conditions to produce the best yield of biodiesel yield on 100 watt microwave power and heating time for 10 minutes. The yield of biodiesel is 93.06%. The laboratory analysis results show five methyl ester compounds (biodiesel) such as methyl myristate, methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate. The physical properties of biodiesel produced have met several criteria of Dirjen Migas no 13438K / 24 / DJM / 2006 for biofuel / biodiesel and SNI 04 - 7182 (2012).

Keywords: biodiesel; physical properties; microwaves; waste cooking oil ; transesterification

1. Introduction

Background

The fossil diesel fuel reserves are depleted and will eventually run out. Biodiesel has the potential to replace diesel fuel, as it can be made from renewable sources, vegetable oils or animal oils. The advantages of using alternative fuels are better emissions, biodegradability, and do not contribute to increasing atmospheric CO2 levels [1]

Biodiesel has several distinct advantages over diesel in the following aspects of security, biodegradability, and environment [2]:

- Renewable fuels with net energy gains to produce them
- Higher flashes that make it safer to transport and store
- Greatly reduces particulate emissions and carbon monoxide
- Reducing Polycyclic Aromatic Hydrocarbons (PAHs) and nitration carcinogenated
- Basically does not contain sulfur, thereby greatly reducing sulfur dioxide emissions from diesel vehicles
- Can decompose as soon as dextrose

Waste cooking oil is often used for frying repeatedly, even until the color is dark brown or black and then discarded. The use of waste cooking oil repeatedly is very dangerous for health. In its use,
waste cooking oil undergoes chemical changes due to oxidation and hydrolysis, which can cause damage to the waste cooking oil. To overcome this, waste of used waste cooking oil (jelantah) can be used as raw material for making biodiesel [3]. Transesterification is a reversible reaction, in which triglycerides change completely into diglycerides, monoglycerides, and finally become glycerin. Stoichiometrically, 3 moles of alcohol is required for 1 mole of triglyceride, but in practice a greater comparative ratio is required to shift the equilibrium resulting in more esters. The transesterification reaction converts triglycerides (96-98% oil) and alcohol to ester, with residual glycerine as a by-product. The result is long and branched triglyceride molecules converted into smaller esters having similar size and properties to diesel oil.

Alcohols used are short chain alcohols, such as methanol, ethanol and butanol. Methanol and ethanol can be easily produced from vegetable materials. Ethanol produces less ethyl ester and leaves a lot of carbon residue. Methanol in addition to its cheaper price, is also the most commonly used type of alcohol. The catalyst is used to speed up the course of the reaction [4].

Methanol and ethanol are the most widely used types of alcohols in the industry, since both types of alcohols give relatively faster reactions. Reactions with alcohols having lower boiling points are carried out at 70-85 ºC, whereas for reactions with high boiling alcohols it is carried out at a temperature of 200-250ºC. The reactor used is cultivated in a dry state and the free fatty acid content present in the oil or fat should be small. The catalyst concentration will be reduced because water and free fatty acids will react with the alkaline catalyst and form the soap.

Methanolysis with 1% by weight of potassium hydroxide (KOH) yields the best conversion with the highest yield and excellent biodiesel viscosity [5]. Stoichiometric reactions require 1 mole of triglyceride and 3 moles of alcohol. However, excess alcohol is used to increase the yield of the alkyl ester and facilitate the phase separation of the formed glycerol [6]. The optimum molar ratio of methanol / oil is 6: 1 [5].

The entire transesterification reaction can be written as follows [7]:

\[
\text{Triglycerides} + 3 \text{CH}_3\text{OH} \xrightarrow{\text{katalis basa}} \text{Biodiesel} + \text{Glycerol}
\]

**Figure 1. Transesterification Reactions [6]**

When the transesterification process has been widely used and becomes important, there are some inefficiency considerations in current transesterification roses. In conventional heating for the transesterification process (batch process, continuous, and supercritical methanol), heat energy is transferred by convection, conduction, and radiation from the surface to the feedstock. Thus, conventional heating consumes more energy and takes longer for preheating and reaction, optimally 1 hour to produce 95% biodiesel yield.

One alternative energy, "microwave irradiation" can be used for the transesterification process. In the spectrum of electromagnetic radiation, the area of microwave radiation lies between infrared radiation and radio waves. Microwaves have a wavelength of 1 mm - 1 m with frequencies between 0.3 - 300 GHz. In general, to avoid interference, microwave equipment is usually set with a 12.2 cm wavelength with a frequency of 2.45 GHz [8]. Microwave heating is more advantageous than conventional method heating, where heating is very slow and inefficient because the transfer of energy to the material depends on the convection currents and the thermal conductivity of the reaction mixture [5].
When the conventional transesterification process takes 75 minutes, the process with a microwave takes only 4 minutes. At the percentage increase in power, in the same time, the number of conversions obtained is somewhat constant. The use of the microwave transesterification process dramatically reduces the reaction time from 75 minutes to 4 minutes, (at 60 ºC) so it saves time. The irradiation time should be controlled to avoid overheating which can destroy some organic molecules. Radiation power levels should not be too high, which can cause damage to organic molecules [2].

Some examples of transesterification methods using microwave irradiation have been performed both batch and continuous. Leadbeater and Stencel have reported the use of microwaves as a quick and simple way of making biodiesel [9]. In this research, biodiesel is made by using batch micro wave.

2. Research methodology
Time And Place Of Research
The research has started from June 2017 until April 2018 with the following stages:

a. Literature studies, discussions and consultations related to topic plans and research titles to be discussed (biomass, biodiesel, new and renewable energy sources).

b. The design of the test equipment is carried out in the Workshop of Engineering & Maintenance Engineering Department of Engineering Polytechnic Negeri Sriwijaya Palembang.

c. Testing, equipment performance test conducted at Energy Conversion Laboratory of Energy Engineering Department Department of Chemical Engineering State Polytechnic of Sriwijaya Palembang and Refinery Unit 3 Pertamina Plaju Laboratory.

Materials and Research Methods
The materials used in this research are walnut oil, activated carbon, methanol (96%), KOH, and aquades. Waste oil obtained from waste cooking oil used stalls around the campus. KOH, hydrochloric acid and sulfuric acid are obtained from Merck. The sterile distilled water is obtained from PT Ikapharmindo. The methanol used has a 96% purity obtained from Brataco Chemika. The main tools used are microwave oven, separator funnel, and magnetic stirrer.

Initial treatment stage
The experiment begins with a bleaching process of waste cooking oil by heating at 70ºC with stirring for 1 hour with 7% by weight of activated carbon. Then the waste cooking oil is filtered with filter paper to remove any remaining debris. Performed measurements of free fatty acid (FFA) in waste cooking oil.

Transesterification process
In the transesterification process, ready-to-use waste cooking oil is put into a beaker glass of 50 grams. Meanwhile, a methanol solution was prepared (methanol molar ratio: oil = 6: 1), which added a KOH catalyst of 1% by weight of waste cooking oil. Then both of them are mixed and stirred evenly in beaker glass and put into microwave oven which have previously been arranged power and time. Transesterification of waste cooking oil takes place in a microwave oven by: (a) variations in microwave power (100, 180, 300, 450, and 600 Watt) at 5 min, and (b) reaction time variation (10, 20, 30, 40 and 50 minutes) at a fixed power of 100 Watt.

The process of separation and purification
After the specified time, then the transesterification result is removed from the oven and transferred into the separation funnel. The product is idle for ± 20 hours to form 2 layers. The top layer is
biodiesel and the bottom layer is glycerol. Then both are separated. The separated biodiesel is washed repeatedly with aquadest until the distilled water no longer contains soap and looks clear.

**Product analysis**
The biodiesel obtained is then weighed to obtain a yield. The biodiesel characteristic test was analyzed to determine the biodiesel physical properties based on the criteria of Director General of Oil and Gas for biodiesel.

**Results and Discussion**
In this study, biodiesel was made using KOH catalyst (1% wt. Waste cooking oil) and 96% methanol in various heating power and heating time. From the measurement results obtained, free fatty acids fatty acid level of 0.5% so that directly can be done transesterification process. Initially the yield of biodiesel obtained will increase as the power and duration of heating increases. However, when optimum heating power and time have been reached, the resulting biodiesel weight gain will decrease. From experiments that have been done we get the optimum biodiesel weight is on 100 Watt heating power and 10 minutes heating time. The results obtained are the golden yellow biodiesel at the top and glycerol are blackish red at the bottom. Once separated and purified by washing with warm aquasions, the resulting biodiesel will be colored kuning bening.

**Effect of heating power on yield (biodiesel)**
Biodiesel results in various power variations with constant time can be seen in table 1 and figure 2.

| Power (Watt) | Weight Biodiesel (gram) | Yield (%) |
|-------------|-------------------------|-----------|
| 100         | 44.60                   | 89.20     |
| 180         | 41.81                   | 83.62     |
| 300         | 37.63                   | 75.25     |
| 450         | 32.40                   | 54.79     |
| 600         | 27.17                   | 54.33     |

![Table 1. Result of Biodiesel Making Experimant with Power Variation (Watt) 5 Minutes](image)

**Figure 2. Graph of Power Relation (watt) with yield Biodiesel (% weight)**

Based on table 1 and figure 2, the yield of biodiesel decreased to 450 watts, then decreased significantly until 600 watts of power. It is seen in this experiment that the optimum biodiesel yield obtained at 100 watts, ie 89.20%.

**Influence of time of heating to yield (biodiesel)**
Biodiesel yield at various time variations with constant heating power can be seen in table 2.
Table 2. Result of Biodiesel Making Experiment with Variation of Time (100 Watt Power)

| Time (minute) | Weight Biodiesel (gram) | Yield (%) |
|--------------|-------------------------|-----------|
| 10           | 46.46                   | 90.00     |
| 20           | 42.35                   | 84.70     |
| 30           | 38.24                   | 76.40     |
| 40           | 34.13                   | 68.10     |
| 50           | 30.02                   | 59.80     |

The transesterification reaction using microwave radiation can speed up the reaction, which conventionally lasts for 1-2 hours. Most conventional transesterification processes are completed in the first 30 minutes of reaction (achieving 80% yield), then completely complete after 1 hour (yield 96.15%). By increasing the reaction time of 3 hours there is no addition of too large yield (yield 96.30%). From the results obtained, the optimum yield percentage was obtained using the molar ratio of methanol: oils of 6:1, the catalyst used KOH (1%) and the temperature of 65 ° C for 1 hour [5].

Based on table 2 it can be seen that the effect of time is very visible at the time under 10 minutes. Before 10 minutes, the percentage of biodiesel produced is quite large compared to the time afterwards. While in the region of 10 to 20 minutes, it may be an optimum region, because after reaching a certain point, the percentage gain of biodiesel decreases again. The optimum biodiesel conversion results were obtained at 10 minutes of radiation, which was 93.00%. As the reaction continues for a longer time, the resulting biodiesel conversion results decrease with the addition of radiation time.

3. Results and Discussion

Analysis of physical properties of biodiesel

To know the biodiesel that has been produced, it is necessary to do some test of biodiesel parameters in accordance with the specification of Director General of Oil and Gas for biodiesel no 13483K / 24 / DJM / 2006 and SNI 04 - 7182 (2012). The biodiesel test includes density, viscosity, flash point, pour point, moisture content that can be seen in table 3 for WVO and table 4 for synthesis.

Table 3. Physical Properties of Biodiesel

| No. | Properties                        | Unit     | Result  | Method            | SNI          |
|-----|-----------------------------------|----------|---------|-------------------|--------------|
| 1   | **Specific Gravity at 60/60 °F**  | g/mL     | 0.9092  | ASTM D 1298       | 0.850 - 0.890|
| 2   | **Kinematic Viscosity at 40 °C**  | mm²/s    | 8.5415  | IKU/5.4/TK-02     | 2.3 – 6.0    |
| 3   | **Flash Point, PM.c.c**           | °C       | 152.0   | IKU/5.4/TK-03     | min. 100    |
| 4   | **Pour Point**                    | °C       | 9       | IKU/5.4/TK-04     | - 15 – 10   |
| 5   | **Water Content**                 | % vol.   | trace   | ASTM D 95         | maks 0,05   |
Table 4. Physical Properties of Biodiesel Result of Synthesis

| No. | Properties                        | Unit  | Result   | Method         | SNI       |
|-----|-----------------------------------|-------|----------|----------------|-----------|
| 1   | Specific Gravity at 60/60 °F      | g/mL  | 0.8669   | ASTM D 1298    | 0.850 - 0.890 |
| 2   | Kinematic Viscosity at 40 °C      | mm²/s | 4.8810   | IKU/5.4/TK-02  | 2.3 – 6.0  |
| 3   | Flash Point, PM.e.c               | °C    | 150.0    | IKU/5.4/TK-03  | min. 100   |
| 4   | Pour Point                        | °C    | 9        | IKU/5.4/TK-04  | - 15 – 10  |
| 5   | Water Content                     | % vol.| trace    | ASTM D 95      | maks 0,05  |

Compared with the requirements of the quality of biodiesel of the Director General of Oil and Gas and the Indonesian National Standard, in terms of density, kinematic viscosity, flash point, and pour point, have fulfilled the stipulated requirements. This biodiesel can therefore be considered as a replacement fuel or additional material for diesel.

4. Conclusion

Specific Gravity or Density is the ratio of the mass amount of a substance to its volume at a certain temperature. The lower the temperature, the biodiesel will be higher and vice versa. The presence of glycerol in biodiesel that may affect the density of biodiesel because glycerol has a high enough density (1.26 g / cm³).

Viscosity is one of the factors affecting the speed of separation of glycerol from biodiesel besides density. Glycerol is one of the compounds that can increase the viscosity of biodiesel. Visuality of the product in each of the lowest catalyst variables when the microwave power of 200 watts. This is because the greater the power will provide a large thermal effect is also characterized by rapid temperature rise. The reactants that have been converted to biodiesel and glycerol will undergo further reactions as pressure increases and temperature increases. While Flash Point does not significantly change or affect the results. Water content can be eliminated by cladding or filtering Microwave microwave (microwave) can be utilized in the manufacture of biodiesel from waste cooking oil through the transesterification process. Making biodiesel by utilizing microwaves requires a much shorter time when compared with conventional biodiesel manufacturing process. The effect of reaction time and microwave power on the product indicates that the greater the time and the heating power, the yield of the resulting product has a tendency to increase to the highest (optimum) point and then to fall back. In general, the quality of biodiesel produced has met the established standards and provisions of biodiesel (SNI). Biodiesel with the largest yield produced at reaction time 10 minutes, 100 Watt power. The optimum yield was 93.00% by weight.

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