Biodiesel production from used frying oil using electrolysis method with methanol addition

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Abstract. An effort that can be carried-out in facing the energy crisis is by developing some new alternative and renewable energy source to reduce the usage of fossil energy, one of those is by producing biodiesel from used frying oil. Biodiesel production in this research is conducted by processing used frying oil using electrolysis process, the electrolysis voltage varies with the addition of methanol. The used frying oil is collected mainly from home industries. The electrolysis reaction lasts for 4 hours with various voltages of 6, 9, and 12 V with various methanol volumes of 20, 30 and 40 ml. The highest yield of biodiesel obtained is 38.3% at 12 V with 20 ml methanol addition. The lowest cetane number is 80.3 at 9 V with 20 ml methanol addition, this number is too high above the standard cetane number for biodiesel which is 51. The only density number of biodiesel produced that meets the standard is 877 gr/cm$^3$ at 9 V with addition of 20 ml methanol or 40 ml methanol. This research requires further study and more parameters to obtain biodiesel which meets the national standard.

1. Introduction
Biodiesel is an alternative fuel that can be obtained from plant oil, animal fat or used oil through esterification with alcohol addition. Biodiesel can be used without re-modification of diesel engine. Biodiesel can be written as B20 which means in the fuel contains 20% biodiesel and 80% diesel oil [1,2].

Biodiesel feedstocks come from plant or animal fat oil, therefore biodiesel is classified as a renewable fuel. Basically all vegetable oils or animal fats can be used as raw materials for making biodiesel. A lot of research has been done to obtain alternative raw material that can be used widely for biodiesel manufacture. Biodiesel mostly derives from palm oil, used frying oil, castor oil, and soybean oil [3,4].

Advantages of biodiesel:
- Biodiesel has characteristic which is similar to diesel oil, so it can be directly used on diesel motors without significant modification with a very small damage risk [5–7].
- Biodiesel provides a better lubrication effect than conventional diesel oil. Even one percent addition of biodiesel in fuel can increase lubrication by nearly 30 percent. The experimental results prove that within 15,000,000 miles biodiesel fuel usage by a motor vehicle provides fuel consumption, horse power, and torque that almost the same as conventional diesel oil [8–10].
Biodiesel can be renewed and its closed carbon cycle does not cause global warming. Life cycle analysis shows that overall biodiesel emissions are 78% lower compared to diesel engines that use petroleum fuel [9], [11–13].

1.1. Cetane number
Cetane number is the parameter used to determine the combustion quality of diesel fuel. Cetane numbers indicates the ease of fuel burning when injected into the engine [14]. The cetane number of biodiesel is minimum 51 while the standard for diesel is 48, that means that the cetane number of biodiesel is 1.05 times higher than diesel. In diesel engine, air is compressed from 30 to 40 kg/cm², the pressure in the combustion chamber during fuel burning rises from 60 to 65 kg/cm² [15–17]. It is expected that the fuel is not burning slowly in order to prevent drastic increase of the chamber pressure, if the pressure is too high then it will ignite explosion.

In biodiesel fuel, the cetane number of 46.95 means that the fuel has a tendency to ignite combustion on a mixture of 46.95 parts of fuel and the rest of 53.05 parts of methyl naphtalene. If the cetane number of biodiesel is 51, then it can be classified as a fast road fuel diesel (fast diesel engine is on cetane number range of 40 to 70). The higher the cetane number the faster the combustion, if the combustion is fast that makes the thermodynamic efficiency higher, in the mean, while the lower number of cetane the lower quality of ignition, this is due to the ignition requires high temperature to start the burning process [17].

1.2. Kinematic viscosity
Standard for kinematic viscosity of biodiesel is of 2.3-6 cSt. If the number of the viscosity is too high, the friction loss in the pipeline will be high, because the pump system will work heavily due to high friction as the result of high viscosity. Besides, high viscosity will also make the filtration process difficult and there is a huge possibility that the dirt will be unfiltered and remains in the oil. Conversely, too low viscosity will result in a thin lubrication, and low lubrication will cause engine weared and damaged [15-18].

1.3. Specific gravity
The specific gravity of biodiesel is the comparison between the biodiesel density and the water density measured at standard pressure and temperature. Specific gravity of biodiesel for diesel ranges between 0.82-0.95 [19].

1.4. Used frying oil
Used frying oil is a kind of oil which has been used for frying process and is categorized as waste. It can damage the environment and can cause a number of serious diseases if it is consumed [20]. During the process of frying, oil experiencing degradation reactions caused by heat, air, and water, resulting in oxidation, hydrolysis, and polymerization reactions [21].

Based on chemical composition, used frying oil contains carcinogenic compounds, which occur during the frying process. So it is clear that the use of sustainable cooking oil can damage human health. The use of cooking oil repeatedly will make cooking oil contains carcinogenic free radicals such as peroxides, epoxides, and others. In experiments involving animals, consumption of foods that are rich of peroxide groups causes various diseases, such as colon cancer. Used frying oil is more viscous than fresh oil because of the formation changes in saturated fatty acids at the time of the frying process. The molecular weight and iodine number decreased while the specific gravity and the sapling rate were higher.

1.5. Electrochemistry
Electrochemistry is the study of electronic aspects and chemical reactions [22]. The elements used in electrochemical reactions are characterized by the number of electrons they possess, in other words, electrochemistry is the study of the relationship between chemical and electrical work, which usually
involves electrochemical cells that apply the principle of redox reactions (oxidation-reduction) in their applications. Electrochemical cells are divided into two based on the reaction, namely:

- Voltaic cells are chemical reactions that take place spontaneously and generate electric current.
- The electrolysis cell is a process that uses electrical energy to prevent nonspontaneous chemical reactions.

Electrochemical reactions involve the transfer of free electrons from a metal to a component in a solution or a medium. Electric movement measurements of an electrochemical cell within a certain temperature range can be used to determine the thermodynamic values of the reaction as well as the activity coefficients of the involved electrolyte. The electrochemical cell is a device used to carry out the above changes. In a cell, electrical energy is generated by electron discharge on an electrode (oxidation) and electron reception at another electrode (reduction). Electrodes that release electrons are called anodes while electrons that receive electrons are called cathodes. So an electrochemical cell always consists of:

- Anode, the electrode where the oxidation reaction takes place.
- Cathode, electrode where reduction reaction takes place.
- Electrolyte solution is an ionic solution which can conduct current and considered as a kind of resistor in a circuit, thus the solution properties that is resistance (R) following Ohm's law.

2. Methodology

2.1. Materials and method

Used frying oil is processed into biodiesel using electrolysis method with variation of electric voltage and methanol ratio. The electrode used in this electrolysis process is graphite. Graphite is an inert electrode, which is often used when unwanted reactions occur on the cathode and anode [4], [23]. The distance of the electrode is set as far as 1.5 cm because the distance between the electrodes affects the amount of electric current that flows during the electrolysis process. The catalyst used in this electrolysis process is NaOH, and it is evenly mixed first with CH₃OH (methanol). The methoxide ions are formed when methanol reacts with the hydroxyl ions which can be seen in equation (1) and the methoxide ions have nucleophilic properties that will attack the carbonyl groups in the triglyceride molecule to form glycerol.

\[ \text{CH}_3\text{OH} + \text{NaOH} \rightarrow \text{CH}_3\text{ONa} + \text{H}_2\text{O} \]  \hspace{1cm} (1)

In the electrolysis process, the mixture of H₂O and NaCl with inert electrodes used will result in chlorine or oxygen gas forming on the anode, hydroxyl ions and hydrogen formed at the cathode. Transesterification of triglycerides with methanol requires methoxide ions to react to form biodiesel. Reaction on the anode:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]  \hspace{1cm} (2)
\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  \hspace{1cm} (3)

Reaction on the cathode:

\[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  \hspace{1cm} (4)

2.2. Electrolysis process

This electrolysis process using graphite as cathode and anode, the electric currents are equal to 6, 9, and 12 V with distance between each electrodes is 1.5 cm, process time is 4 hrs and using magnetic stirrer with 30 rpm rotation.

- Set the power supply switch selector on the DC voltage position and select the measuring limit of the voltage.
• Connect the positive cable from power supply to AVO meter and negative cable to anode graphite. Connect the cable from the AVO meter to the cathode graphite.
• Mix NaOH (1% wt of oil) and methanol until all of NaOH is dissolved. The amounts of methanol are 20, 30, and 40 ml.
• Mix NaCl (0.56 wt% of oil) and aquadest (2% wt of oil) until the whole NaCl dissolves.
• Mix methanol and NaOH with salt solution (NaCl and aquadest) into 150 ml of cooking oil in a beaker glass.

After the electrolysis process completed, leave it for 24 hrs, afterwards biodiesel produced can be separated using separator funnel. The resulting biodiesel is then washed with a heated aquadest at 50°C, wait until it forms two layers, use separation funnel to separate them. Do this for several times until the last wash looks clean. Place biodiesel into oven with temperature of 110°C for 2 hours to reduce water content. Last step taken is analysing the biodiesel produced.

![Device for electrolysis process](image)

**Figure 1.** The device for electrolysis process

### 3. Results and Discussions

| Used frying oil (ml) | Methanol (ml) | Voltage (V) | Yield (%) |
|----------------------|--------------|-------------|-----------|
| 6                    | 31.2         | 9           | 5.30      |
| 20                   | 38.3         | 12          | 33.4      |
| 12                   | 26.2         | 6           | 35.7      |
| 100                  | 11.3         | 30          | 6.20      |
| 40                   | 12           | 9           |           |

*Table 1. Percentage of biodiesel produced (yield)*
Figure 2. Percentage of biodiesel produced (yield) with various voltages and methanol addition

Based on the result shown on figure 2, the highest yield of biodiesel obtained is 38.3% at 12 V with 20 ml of methanol addition. Thus the minimum required voltage in the chlorine gas formation process is 2.19 V which is calculated based on the reaction occurring on the cathode and anode. The higher the voltage applied, the greater the chlorine gas produced.

\[
\text{Cathode: } 2\text{H}_2\text{O(l)} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(\text{aq}) \quad E^0 = -0.83 \text{ V} \tag{5}
\]

\[
\text{Anode: } 2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(g) + 2 \text{ e}^- \quad E^0 = -1.36 \text{ V} \tag{6}
\]

\[
2\text{H}_2\text{O(l)} + 2 \text{Cl}^-(\text{aq}) \rightarrow \text{H}_2(g) + 2\text{OH}^-(\text{aq}) + \text{Cl}_2(g) \quad E^0 = -2.19 \text{ V} \tag{7}
\]

The hydroxyl ion (OH\(^-\)) produced will also increase with the increase of the voltage applied to the electrolysis process. Methoxide ions are formed when methanol reacts with hydroxyl ions so that by increasing the voltage then the methoxide ions formed will be higher and the yield of biodiesel produced will also increase.

| Table 2. Cetane number of biodiesel produced |
|---------------------------------------------|
| Used frying oil (ml) | Methanol (ml) | Voltage (V) | Cetane number |
|----------------------|---------------|-------------|---------------|
| 6                    | 84.3          | 6           |               |
| 20                   | 9             | 80.3        |               |
| 12                   | 87.3          | 6           | 80.4          |
| 100                  | 30            | 9           | 92.0          |
|                      | 12            | 87.8        |               |
|                      | 6             | 82.0        |               |
|                      | 40            | 9           | 84.6          |
|                      | 12            | 84.4        |               |
Figure 3. Cetane numbers of biodiesel produced with various voltages and methanol additions

Based on the result shown in figure 3, cetane numbers of biodiesel produced are much higher than Indonesian National Standard (SNI) which is 51 [19], [24]. The highest cetane number obtained is 92.0 at 9 V with 30 ml methanol addition, the lowest cetane number is 80.3 at 9 V with 20 ml methanol addition. Cetane number seems to increase along with higher voltage and the addition of methanol volume.

Table 3. Density of biodiesel produced

| Used frying oil (ml) | Methanol (ml) | Voltage (V) | Density (gr/cm³) |
|---------------------|---------------|-------------|------------------|
| 20                  | 6             | 6           | 683              |
|                     | 9             | 9           | 877              |
|                     | 12            | 12          | 904              |
| 100                 | 30            | 6           | 793              |
|                     |               | 9           | 897              |
|                     |               | 12          | 904              |
|                     |               | 6           | 683              |
|                     |               | 9           | 877              |
|                     |               | 12          | 686              |

Figure 4. Density of biodiesel produced with various voltages and methanol additions
Almost all of density numbers of biodiesel produced do not meet the SNI standard which is in the range of 850-890 [19,24]. The only density number that meets the SNI standard is 877 gr/cm$^3$ at 9 V with addition of 20 ml methanol or 40 ml methanol. The biodiesel density is influenced by the length of the fatty acid chain constituent. The high density indicates that the resulting methyl ester still has a long fatty acid chain. Cooking oil has a high content of linoleic acid. Linoleic acid is considered a long chain fatty acids, so that cooking oil is usually has a high density.

| Table 4. Kinematic viscosity of biodiesel produced |
|-----------------------------------|----------|----------|-------------------|
| Used frying oil (ml) | Methanol (ml) | Voltage (V) | Kinematic viscosity (cSt) |
|-----------------------|--------------|-------------|--------------------------|
| 6                     | 44.654       | 20          | 43.851                   |
| 9                     | 43.285       | 12          | 43.416                   |
| 12                    | 43.198       | 6           | 42.691                   |
| 100                   | 30           | 9           | 39.763                   |
| 40                    | 34.218       | 12          | 17.086                   |

Figure 5. Kinematic viscosity of biodiesel produced with various voltages and methanol additions

None of the kinematic viscosity of the biodiesel produced that meets the SNI standard which is in the range of 2,3-6,0 cSt [19], [24]. All of them are above 17 cSt, these results are assumed as the influence of incomplete transesterification of used cooking oil.

4. Conclusions
The more methanol volume used, the lower yield of biodiesel obtained. Therefore it is not necessary to add the volume of methanol into the electrolysis process, because the addition of methanol over 20% of the material gives negative impact to the process.

The higher the voltage current used in the electrolysis process the more biodiesel yield is obtained because higher voltage in the electrolysis may have positive contribution to the process.
The usage material with a low viscosity resulting to kinematics viscosity of oil production which meets the Indonesian National Standard (SNI). Therefore it is crucial to reduce the viscosity of used cooking oil prior to electrolysis process.

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