SYNTHESIS OF BIODIESEL FROM CRUDE PALM OIL BY USING CONTACT GLOW DISCHARGE ELECTROLYSIS

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Abstract

This research has evaluated the use of Contact Glow Discharge Electrolysis method in the synthesis of biodiesel. The purpose of this research is to get the synthesis process and biodiesel product. The solution used is the mix of Crude Palm Oil and methanol with molar ratio of 1:24, and catalyst of NaOH and KOH with variation of concentration 0.5% - 1.5%-wt. The result shows that the biodiesel can be made from transesterification reaction that may be initiated by radical methoxide. The use of electrolyte KOH is better than NaOH based on the yield of biodiesel and the energy consumption. The optimum yield reaches 97%, at the synthesis for 30 minutes with the use of KOH 1%-wt with the energy consumption of 1.32 kJ/mL.

Keywords: Biodiesel; Contact Glow Discharge Electrolysis; hydroxil radical.

Introduction

Conventional synthesis of biodiesel from Crude Palm Oil (CPO) commonly uses the transesterification method or alcoholysis of triglycerides by using a homogeneous catalyst NaOH or KOH. Base catalyst in the production process of biodiesel plants is the most commonly used because the process is fast and easy to do. However, this process has disadvantage which the reaction of saponification produces much soap and water. Moreover, this method has a slow reaction rate and the reaction stops before the 100% of feedstock is converted into biodiesel [1].

To fasten the reaction rate and avoid the formation of soap and water, this research uses a new method, which is Contact Glow Discharge Electrolysis (CGDE). CGDE is an electrochemical process in which plasma is generated by DC current between the electrodes and the electrolyte surface in the vicinity [2]. CGDE is one of plasma electrolysis methods that is very prolific producing hydroxyl radical (HO•) [3]. The hydroxyl radicals are supposed to react with methanol and form methoxy radical (CH$_3$O•). The methoxy radicals are believed to react with triglycerides and form biodiesel. The basic principle is to maximize the production of hydroxyl radicals from electrolysis and then they will trigger the transesterification reaction without saponification reaction that forms soap [4]. Other main products of this process are the formation of hydrogen and oxygen gas which are much higher than the Faraday electrolysis process can do so that it is more environmentally friendly [5]. These two advantages can address the problems caused by the conventional method of biodiesel synthesis. In other words, this study can be an alternative method recommendation.
that is much better in the synthesis of biodiesel. At the end, it is expected to be a leading alternative method in the development of biodiesel industry in the future.

**Experimental**

The main tool in this study is a single anode Contact Glow Discharge Electrolysis (s-CGDE) batch reactor (adapted from Saksono [6]) with volume of 2 L. The series of reactor can be seen in Figure 1. The stirring uses a magnetic stirrer with the addition of baffles in the reactor. The function of baffles is to create a more perfect stirring. The reactor is equipped with cooling flow so the temperature inside the reactor can be maintained at 50-60°C.

![Single Anode Contact Glow Discharge Electrolysis Batch Reactor](image)

**Figure 1 Single Anode Contact Glow Discharge Electrolysis Batch Reactor**

*Crude Palm Oil* (CPO) that is used comes from a commercial product manufactured in Indonesia, while methanol (99.9% vol) is used as the transesterification agent. The molar ratio of CPO and methanol is 1:16 and 1:24. NaOH and KOH are used as transesterification reaction catalysts as much as 0.5% - 1.5% and 0.5% - 1% by weight of CPO, respectively. NaOH and KOH are also needed to increase the conductivity of the solution so that plasma can be generated.

**Results and Discussion**

**Current-Voltage (I-V) Characteristics**

Figure 2 shows current-voltage curves that are obtained from experiment of CPO-methanol-NaOH solution with CPO-methanol molar ratio of 1:16 and 1:24. Zone A (Point A1 and A2) is an electrolysis zone where the increase of voltage is proportional to the increase of current. Point B1 and B2 are the points where the plasma begins to appear, which are at 260 V, 0.89 A and 280 V, 0.65 A for molar ratio of 1:16 and 1:24, respectively. C1 and C2 are areas where the increase of plasma intensity is in line with the decrease of electric current; Point D1 and D2 are the points with the lowest current, which are at 700 V, 0.22 A and 740 V, 0.27 A for molar ratio of 1:16 and 1:24, respectively. Furthermore, the increase of voltage is accompanied by the increase of electric current and plasma is brighter. When the methanol content increases, the electrical current will decrease along the curve (Figure 2). This shows that methanol lowers the solution conductivity.
Effect of NaOH and KOH concentration to Biodiesel Production

Table 1 shows that the solution with NaOH electrolyte concentration of 0.5% produces the highest yield compared to the concentration of 1% and 1.5%. This proves that the concentration of electrolytes is not proportional to the yield of biodiesel. The highest yield, which is 79%, is reached at the NaOH concentration of 0.5% with the synthesis duration of 30 minutes. The higher yield can be achieved when the duration is longer for the transesterification reaction will become more perfect.

Table 1 Yield of Biodiesel from Experiments with CPO:Methanol Ratio of 1:16 after 30 minutes of synthesis

| Sample Solution               | Yield (% v/v) |
|-------------------------------|---------------|
| CPO-Methanol + 0.5% NaOH      | 79%           |
| CPO-Methanol + 1.0% NaOH      | 73%           |
| CPO-Methanol + 1.5% NaOH      | 73%           |
| CPO-Methanol + 0.5% KOH       | 95%           |
| CPO-Methanol + 1.0% KOH       | 97%           |

Table 2 also shows that the yield of synthesis using KOH electrolyte is much higher than the yield of synthesis using NaOH electrolyte because the reactivity and solubility of KOH in methanol is greater than NaOH in methanol. KOH is more reactive to form methoxyl which leads to the formation of biodiesel. Additionally, KOH is more active to form of hydroxyl radicals that take a role in breaking the chains of triglycerides.

Acid Number and Free Fatty Acid Content of Biodiesel Products

Acid Number is the mass of potassium hydroxide (KOH) in miligrams that is needed to neutralize a gram of chemical substance. Meanwhile, free fatty acid (FFA) content is the amount of free fatty acid in biodiesel as the result of the hydrolysis reaction. According to the Indonesian National Standard (SNI) [8], the allowable maximum limit of the acid number is 0.8 mg KOH/g with FFA content as much as 0.02% by weight.
The test results of acid number and FFA content in Table 2 indicate that the solution with 1.5% NaOH gives the lowest acid number and FFA content, which are 0.0019 and 0.0001, respectively. The tests show that all samples have values far below the maximum limit required in Indonesian National Standard (SNI).

### Table 2 Chemical and Physical Characteristics of Biodiesel Products from Experiments with CPO:Methanol Ratio of 1:16 after 30 minutes of synthesis

| Sample Solution         | Acid Value (mg KOH/g) | FFA content (%-wt) | Density (g/mL) | Viscosity (cSt) |
|-------------------------|-----------------------|--------------------|----------------|-----------------|
| CPO-Metanol + 0.5% NaOH | 0.00056               | 0.0003             | 0.872          | 5.407           |
| CPO-Metanol + 1.0% NaOH | 0.0037                | 0.002              | 0.846          | 4.055           |
| CPO-Metanol + 1.5% NaOH | 0.0019                | 0.001              | 0.876          | 3.898           |
| CPO-Metanol + 0.5% KOH  | 0.00056               | 0.0003             | 0.864          | 4.589           |
| CPO-Metanol + 1.0% KOH  | 0.00037               | 0.0002             | 0.865          | 5.375           |

**Density dan Viscosity of Biodiesel Products**

The test results indicate the lowest viscosity value, which is 3.898 cSt, is achieved on sample of CPO-methanol with 1.5% NaOH (Table 2). According to Indonesian National Standard (SNI), density of biodiesel should be in the range of 0.850 to 0.890 g/mL, while viscosity of biodiesel should be in the range of 2.3 to 6.0 cSt. The test results show that all samples meet the requirements of SNI.

**Characterization of Methyl Ester in Biodiesel Products**

Sample is analyzed using GCMS. The samples are biodiesel product from experiment using 1% NaOH and KOH electrolytes after 30 minutes of synthesis. The results are obtained in the form of chromatogram signal peaks as shown in Figures 3 and 4. The peaks represent as compound names and compositions in biodiesel sample as shown in Table 3.

Table 3 shows that the total methyl ester contents in biodiesel products reach 99.89% and 99.8% when using NaOH and KOH electrolytes respectively. The products are dominated by Pentadecanoic acid methyl ester (Methyl pentadecanoate) and Octadecenoic acid methyl ester (Methyl octadecenoate). The results are in accordance with the feedstock content which is dominated by palmitic acid and oleic acid.
Figure 3 Characterization of Biodiesel from Experiments of CPO + Methanol + 1% wt NaOH by using GCMS

Figure 4 Characterization of Biodiesel from Experiments of CPO + Methanol + 1% wt KOH by using GCMS
Table 3 Methyl Ester Composition in Biodiesel Products

| No. | Compound Name                  | Composition (%-wt) | CPO-Methanol-1% wt NaOH | CPO-Methanol-1% wt KOH |
|-----|--------------------------------|--------------------|-------------------------|------------------------|
| 1   | Octanoic Acid Methyl Ester     | 0.02               | 0.02                    |                        |
| 2   | Decanoic Acid Methyl Ester     | 0.02               | 0.02                    |                        |
| 3   | Dodecanoic Acid Methyl Ester   | 0.29               | 0.29                    |                        |
| 4   | Tetradecanoic Acid Methyl Ester| 1.47               | 1.43                    |                        |
| 5   | **Pentadecanoic Acid Methyl Ester** | **26.42**     | **26.27**               |                        |
| 6   | Hexadecanoic Acid Methyl Ester | 0.55               | 0.23                    |                        |
| 7   | **Octadecanoic Acid Methyl Ester** | **69.94**     | **56.01**               |                        |
| 8   | Eicosanoic Acid Methyl Ester   | 1.16               | 1.14                    |                        |
| 10  | Tetradecanoic Acid Methyl Ester| 0.02               | -                       |                        |
| 11  | Pentanoic Acid Methyl Ester    | -                  | 0.05                    |                        |
| 12  | Palmitoleic Acid Methyl Ester  | -                  | 0.27                    |                        |
| 13  | Octadecadienoic Acid Methyl Ester | -                | 13.98                   |                        |
| 14  | Docosanoic Acid Methyl Ester   | -                  | 0.08                    |                        |
| 15  | Tetracosanoic Acid Methyl Ester| -                  | 0.01                    |                        |

Total | **99.89** | **99.80** |

Figure 5 Energy Consumption at Various CDGE Samples with CPO:Methanol ratio of 1:16 in 30 minutes process

Specific Energy Consumption of Biodiesel Synthesis Using CGDE

The efficiency of the process can be measured from the amount of electrical energy consumed divided by volume of biodiesel produced. Figure 5 shows that the specific energy consumption of the solution using NaOH is a higher than using KOH. This is due to the yield of biodiesel produced using NaOH is lower than using KOH (Table 1). An increase of NaOH concentration in the solution will increase the specific energy consumption because it will increase the electric current due to the increased of solution conductivity. Besides, a low...
concentration of NaOH (0.5%) will produce the highest yield among the other higher concentrations of NaOH (Table 1). The highest specific energy consumption is achieved when using 1.5% wt NaOH, which is of 3.13 kJ per mL (Figure 5). The lowest specific energy consumption is achieved when using 1% KOH for 30 minutes, which is 1.32 kJ/mL. It is slightly higher than specific energy consumption of conventional methods, which is 1.17 kJ/mL [7].

Conclusions

This study has successfully produced biodiesel from CPO using CGDE method where the quality meets the requirement of Indonesian National Standard (SNI) in terms of acid number, free fatty acid content, density, and viscosity. The highest yield is 97% with methyl ester content reaches 99.8%, obtained from CPO-methanol solution with mole ratio of 1:16 and the addition of 1% KOH for 30 minutes process duration. In this condition, the specific energy consumption is 1.32 kJ/mL which is the lowest value in this experiment. It is slightly higher than the specific energy consumption of conventional methods, which is 1.17 kJ/mL.

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