The comparison of cathodic and anodic plasma electrolysis performance in the synthesis of biodiesel

N Saksono1*, J J C Pranata1, Y Muharam1, and Harianingsih 1,2
1Departement of Chemical Engineering, Universitas Indonesia, Kampus Baru UI. Depok 16242, Indonesia
2Departement of Chemical Engineering, Universitas Negeri Semarang, Kampus Sekaran, Semarang 50229, Indonesia

Email: nelson@che.ui.ac.id

Abstract. Synthesis of biodiesel using plasma electrolysis is very promising. This study aims to understand the differences between cathodic and anodic plasma performance in synthesizing biodiesel from palm oil. The raw materials used were palm oil, methanol, and KOH catalyst. In the present study, the effects of the type of plasma and the depth of an electrode for biodiesel synthesis were evaluated. The results show that cathodic plasma gave the highest yield of 98.76% and the lowest specific energy consumption of 720 J/ml. Meanwhile, under the same conditions, the anodic plasma gave the highest yield of 96.09% and the lowest specific energy consumption of 910 J/ml. These results indicate that cathodic plasma is better than anodic plasma in synthesizing biodiesel because it gives higher yield and lowers specific energy consumption.

1. Introduction

The synthesis of biodiesel using the plasma electrolysis method is a breakthrough because it can accelerate the rate of synthesis and lower specific energy consumption compared to the conventional methods. Plasma produces a large amount of methoxyl radical (CH₃O•) that will react to triglycerides to form biodiesel [1]. Plasma electrolysis process begins with gas formation at the anode and cathode [2]. In such a large scale system, materials of anode and cathode are very important as fundamental characteristics [3]. In our previous research, biodiesel has been synthesized using the anodic plasma electrolysis method [4].

This process could produce reactive species in the anode [5]. Plasma can be formed in either cathodic or anodic, depends on the type of electrode [6]. In general, plasma is more stable and easily formed in the cathode than the anode because the cathode emits more secondary electrons[7]. This study aims to investigate the effect of cathodic and anodic plasma performance on biodiesel synthesis from palm oil. Initially, methanol is mixed with potassium hydroxide to produce species, as shown in equation 1 [8]. The high-energy electrons produced by the plasma will break the water molecules into radicals and transform methoxyl ions into methoxyl radicals in the particular electrode [1]. However, a conventional electrolysis reaction will take place in other electrodes in which plasma does not exist [9]. Using cathodic plasma, the reactions in Equations 2 and 3 occur in the cathode while the reaction in equation 4 occurs in the anode. Further, using anodic plasma, reactions in equations 2 and 3 are in anode and reaction in equation 5 is in cathode.
\[ \text{CH}_3\text{OH}_{(aq)} + \text{KOH}_{(aq)} \rightarrow \text{CH}_3\text{O}^-_{(aq)} + \text{K}^+_{(aq)} + \text{H}_2\text{O}_{(l)} \]  
(1)

\[ \text{H}_2\text{O}_{(l)} + e^- \rightarrow \text{H} \cdot + \text{OH} \cdot + e^- \]  
(2)

\[ \text{CH}_3\text{O}^-_{(aq)} + e^- \rightarrow \text{CH}_3\text{O} \cdot + e^- \]  
(3)

\[ 2\text{H}_2\text{O}_{(l)} \rightarrow 4\text{H}^+_{(aq)} + \text{O}_2(d) + 4e^- \]  
(4)

\[ 2\text{H}_2\text{O}_{(l)} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) \]  
(5)

The methoxyl radicals produced by those reactions will attack triglycerides from palm oil to produce methyl esters [10]. In general, the mechanism consists of three stages as shown in figure 1 [11]. The first stage is a nucleophilic alkoxide attack producing tetrahedral intermediate. The second stage is the formation of alkylester and anion diglyceride. The third stage is the regeneration of the active species that will react with the second molecule of the other alcohol followed by the recovery of the base catalyst.

**Figure 1.** The possible mechanism of biodiesel synthesis using plasma electrolysis.

2. **Materials and methods**

2.1. **Materials**

The palm oil used in this study was a commercial cooking oil product in Indonesia. Methanol (analytical grade, Merck) and Potassium hydroxide (Merck) were used as transesterification agent and catalyst, respectively. Water was applied for the cooling process.

2.2. **Instrumentation**

The main equipment in this research was a 2-liter Plasma Electrolysis batch reactor similar to the one used in the previous research [12]. The reactor scheme can be seen in figure 2. The difference is the type of charge given to the tungsten as the electrode where the plasma is formed. When the tungsten is given a negative charge, it will act as a cathode. Contrarily, when a positive charge is given, it will act as an anode. Stirring used a magnetic stirrer with the addition of baffles inside the reactor. Baffles were used to make stirring more effective. The reactor was equipped with a coolant stream to maintain the temperature inside the reactor at 40°C to reduce the possibility of methanol evaporation from the solution.

Tungsten electrode and stainless steel electrode were given negative and positive charges respectively when the reactor would be used as a cathodic plasma reactor. Meanwhile, the tungsten electrode and stainless steel electrode were given positive and negative charges respectively when the reactor would be used as an anodic plasma reactor.
Figure 2. Plasma reactor, 1: Thermometer, 2: Electrode (tungsten), 3: Electrode (stainless steel), 4: Sample hole, 5: Cooling jacket, 6: Magnetic stirrer, 7: Stirrer, 8: Baffle. [12]

2.3. Methods
Potassium hydroxide and palm oil with a ratio of 1:100 were dissolved with methanol. The mixture was then mixed and stirred with oil in a ratio of 1:24 in both reactors until the homogeneous phase was obtained. The electric current applied at the desired voltage so that the plasma was formed and the reaction occurred for an hour.

3. Results and discussion
3.1. Current-Voltage (I-V) characteristics
Some text, figure 3 shows voltage-current profiles from a mixture of palm oil and methanol with a 1:24 molar ratio plus potassium hydroxide as much as 1 wt% of palm oil in experiments with cathodic and anodic plasma.

Zone A is an area of Faraday electrolysis where voltage is proportional to current while Zone C is an area where a gas shield is formed on the electrode surface [12,13]. This gas shield reduces the contact area between the electrode and electrolyte solution so that the current falls. In this zone, spark as a phenomenon of excited electrons also begins to appear [13]. Point B1 and B2 are the points at which the gas shield starts to form, also known as breakdown voltage (V_B). V_B of anodic plasma is lower than V_B of cathodic plasma (V_B1 < V_B2) which means that a gas shield is more easily formed in anode than cathode[14]. On the other hand, V_D (Mid-point Voltage) of anodic plasma is higher than V_D of cathodic plasma (V_D1 > V_D2) which means that plasma was easier to achieve stability in the cathode than in the anode. It was due to the most energy in the anodic plasma was used to evaporate the solution around the anode. However in cathodic plasma, the most energy was used by electrons to support the kinetic energy to excite and form the plasma faster to obtain stability [5,16]. The value of Townsend secondary electron emission coefficient (γ) for the cathode and anode differs very significantly. The value of γ was about 0.01-0.1 for the cathode metal and 0.0001-0.001 for the electrolyte solution around the anode. The negative electrode (cathode) was surrounded by many positive ions. The positive ions made not only the primary electron but also the secondary electrons were emitted [3,5]. Therefore, secondary electron emission occurred more at cathode than at anode. The more excited the electrons are, the easier the plasma will achieve stability.
Figure 3. Voltage-current profile on the solution of palm oil-methanol-KOH using cathodic and anodic plasma

3.2. The effect of electrode depth on biodiesel synthesis

The experiment was conducted by varying the cathode and anode depth of 0.5 cm, 1.5 cm, and 3.5 cm. The result shows that the deeper electrode would increase hydrostatic pressure, hence gas could reach the surface easily and the higher evaporation energy was required to maintain the size of the gas shield as shown in table 1 [14].

| Plasma   | Depth (cm) | Yield (%) | Biodiesel Volume (ml) | Energy (Joule) | Specific Energy Consumption (J/ml) |
|----------|------------|-----------|-----------------------|----------------|-----------------------------------|
| Cathodic | 0.5        | 88.54     | 622                   | 465833         | 749                               |
|          | 1.5        | 92.81     | 652                   | 477310         | 732                               |
|          | 3.5        | 98.76     | 694                   | 499339         | 720                               |
| Anodic   | 0.5        | 92.95     | 653                   | 528264         | 809                               |
|          | 1.5        | 94.15     | 661                   | 597168         | 903                               |
|          | 3.5        | 96.09     | 675                   | 613872         | 910                               |

The increase in energy is marked by the increase of current and brighter plasma. A deeper electrode includes brighter plasma as shown in figure 4. It could enhance the interaction between plasma and other reactants to produce more radicals which initiate the reaction continually so that the conversion increased[15]. Further, this was demonstrated by the increase of biodiesel volume and yield as shown in table 1.
Figure 4. Cathodic plasma at depth of (a) 0.5 cm; (b) 1.5 cm; and (c) 3.5 cm

The specific energy consumption of biodiesel synthesis could be measured by the amount of electric energy consumed divided by the volume of biodiesel produced. The specific energy consumption of anodic and cathodic plasma was 720-749 J/ml and 809-910 J/ml, respectively as shown in table 1. This energy formed by the plasma method was lower than the conventional method (1168 J/ml) which is in line with previous research [13,16].

Table 1 exhibits the volume of biodiesel increased by 11.6% as the cathode depth increased (from 0.5 to 3.5 cm) while its energy consumption increases by 7.2%. It caused a decrease in specific energy consumption. However, in anodic plasma, the volume of biodiesel increased by only 3.4% and its energy consumption increased by 16.2% as the anode depth increased. The increase in energy consumption in anodic plasma was higher than cathodic plasma [17]. Its plasma was easier to achieve stability at cathode than anode as depicted in the characteristics of voltage currents in figure 3 [18].

Figure 5. (a) Cathodic plasma and (b) anodic plasma; at depth of 0.5 cm, 600 volt

There was a significant increase in biodiesel volume (694 ml) while using cathodic plasma for 3.5 cm depth and it was relatively higher than biodiesel volume formed by anodic plasma (675 ml). It was probably due to the larger and brighter plasma formed by cathodic plasma than anodic plasma in figure 5. Furthermore, the lighter plasma indicates that the number of reactive species (i.e. methoxyl radical) for biodiesel production increased [19].

3.3. Biodiesel product characterization

The samples were analyzed using gas chromatography. The peaks shown in table 2 represent the compound names and compositions in the samples in general, there was no significant difference in
product composition which was synthesized by cathodic and anodic plasma in the varying depth of electrodes. The products were dominated by Hexadecanoic acid, methyl ester (methyl palmitate), (Z)-octanes-9-enoic acid, and methyl ester (methyl oleate). However, other compounds such as water and free fatty acid were also detected. These products depended on the natural compounds of feedstock which was dominated by palmitic acid and oleic acid. It also shows that the reaction mechanisms of biodiesel synthesis by using cathodic plasmas are relatively similar. Both cathodic and anodic plasmas were able to convert methanol to methoxyl radicals which initiated biodiesel production.

Table 2. Methyl ester composition in biodiesel products.

| No | Compound Name                        | Cathodic Plasma Depth | Anodic Plasma Depth |
|----|--------------------------------------|-----------------------|--------------------|
| 1  | Tetradecanoic acid, methyl ester      | 0.70                  | 0.73               |
| 2  | Hexadecanoic acid, methyl ester       | 27.44                 | 28.04              |
| 3  | Heptadecanoic acid, methyl ester      | 14.99                 | 15.38              |
| 4  | Octadecanoic acid, methyl ester       | 0.00                  | 3.25               |
| 5  | (Z)-octadec-9-enoic acid, methyl ester| 36.86                 | 34.87              |
| 6  | (9Z,12Z)-octadeca-9,12-dienoic acid, methyl ester | 8.19 | 9.17 |
| 7  | Eicosanoic acid, methyl ester         | 0.29                  | 0.00               |
| 8  | Tetracosanoic acid, methyl ester      | 0.07                  | 1.49               |
|    | **Total**                             | **88.54**             | **92.95**          |

4. Conclusion
This research has successfully investigated biodiesel production using cathodic and anodic plasma formation. Anodic plasma was more easily formed than cathodic plasma, but plasma achieved stability faster in cathodic plasma. The highest biodiesel yields of cathodic and anodic plasma were 98.76% and 96.09%, respectively. The specific energy consumptions of cathodic and anodic plasma were 720 J/ml and 910 J/ml respectively. The low specific energy consumption of cathodic plasma was heavily caused by the lower energy consumption, which was 499.339 kJ while the anodic plasma reached 613,872 kJ. Gas chromatography test results show that there is no significant difference between product composition in cathodic and anodic plasma.

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