Biodiesel synthesis in DBD plasma reactor using triglyceride-methanol mixture contacted with CO\textsubscript{2}-steam gas mixture

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Abstract. The conventional method of biodiesel synthesis is known to have a few drawbacks. With the intent of reversing the drawbacks, a research on biodiesel synthesis from triglycerides and methanol using cold plasma Dielectric Barrier Discharge (DBD) reactors was conducted by using two types of plasma carrier gas, namely argon (Ar) and a mixture of Ar + CO\textsubscript{2} + H\textsubscript{2}O (vapor) by varying the temperature and reaction time systematically. The major products obtained from the cold plasma dielectric barrier discharge (DBD) reactor consists of four primary components: FAME (fatty acid methyl ester) or biodiesel, alkane (paraffin) and fatty alcohol and/or other side products which were analysed using GC-MS and FT-IR. The analysis was carried out mainly to determine the chemical conversion associated with reactant or biodiesel products. The types of triglycerides used in this research are (a). used cooking oil, (b). used mixtures of used palm oil and fresh palm oil, and (c). used mixtures of used palm oil and fresh castor oil. With the synthesis time for 2 hours, it was found that the cold plasma DBD reactor was able to change about 47-89 % mixture of triglycerides (without catalyst and excess methanol) to various product such as FAME, greendiesel paraffin and fatty alcohols. It seems the uses of Argon Gas produce a 23.7% higher yield of FAME and paraffin than the mixture of argon and CO\textsubscript{2}.

1. Introduction
The conventional biodiesel synthesis method (FAME, fatty acid methyl ester) converts triglycerides (vegetable oil) and alcohol (methanol or ethanol) using a chemical catalyst (NaOH or KOH) through a transesterification reaction. However, the transesterification reaction requires a high molar ratio of alcohol to triglycerides and the presence of a chemical catalyst. This method is still facing various problems, especially (a). glycerine formation as a by-product, (b). the mixture becomes corrosive, and (c). the separation process of catalyst and side products is quite complicated [1].

In this study, an alternative method for the synthesis of diesel engine fuels was proposed by using plasma. In short, it can be explained that biodiesel (other diesel engine fuel) is synthesized with the help of plasma fields as a catalyst, that is, from the type of cold plasma Dielectric Barrier Discharge (DBD) reactor. From previous studies, it was reported that DBD reactor can be used to synthesize biodiesel from palm oil and methanol without the formation of glycerin by-products, without soap formation, and without the use of homogeneous or heterogeneous catalysts [2,3,4]. For this purpose, the built-in cold plasma DBD reactor system prototype will be conditioned in such a way as to ensure the best conversion rate is obtained. This study also aims to analyze the typical effects of various reaction parameters, such as the type of triglycerides, plasma carrier gas, and reaction time for the biodiesel production process.

2. Material and Methods
2.1 Materials and Equipment

There are three kinds of sources of triglycerides, namely (a) palm oil cooking oil, (b) a mixture of 50:50% w/w used palm oil and fresh palm oil, and (c) 50:50% w/w mix of used palm oil and castor oil. Each of the three types of triglyceride was then dissolved with 10% w/w in Indonesian premium liquid diesel engine fuel (Pertamina DEX) and methanol as reactants. The plasma carrier gas used can be pure argon (Ar) gas and a mixture of 50:50 v/v carbon dioxide (CO₂) and Ar being moistened with water vapor (H₂O). Figure 1 shows the experimental set of this study.

![Diagram](image)

**Figure 1.** Schematic design of DBD plasma reactor with cylindrical electrodes

1 Power Source  8 DBD Reactor
2 Slide Regulator  9 Check Valve
3 Transformator  10 Flow Meter
4 Voltmeter  11 Check Valve
5 NST/EPT  12 Check Valve
6 Peristaltic Pump  13 Gas (Argon and CO₂)
7 Magnetic Stirrer

The cold plasma DBD reactor used consists of a 300 mm quartz glass cylinder tube with a diameter of 18 mm which wrapped a spiral (coil) SS-304 as an outer electrode, and an SS-304 tube in a quartz tube as an inner electrode (high voltage). The reactor is raised by 5 degrees to make room for plasma carrier gas and operates in such a way as to form a pulse reactor. The plasma produced by an Energy Power Transformer (EPT) 10 kV 30 mA uses 1-phase AC 220 V. Figure 2 shows the DBD plasma reactor used in this research.
2.2 FAME preparation and procedure
The temperature of the mixture (reactant liquid) used was heated to 40 °C before being added to the plasma reactor. The feed is inserted into the DBD reactor at 1.33 mL/s while the gas (plasma carrier) is introduced into the reactor by setting the flow rate of 25.27 mL/s at atmospheric pressure. The reactor system, voltage, gas and liquid flow rate are kept constant. The reaction time is 120 minutes, with sampling every 60 minutes to be analyzed using GC-MS for identification of FAME (ASTM E202), and FT-IR analysis for identification of the molecular structure of synthesis products (ASTM E168). Other analysis of important biodiesel characteristics is also carried out, which are: density (ASTM D1298) and viscosity (ASTM D445).

3. Results and Discussion
3.1 Effect of Triglycerides Sources on Biodiesel Yield
Optimizing the selection of raw materials in the synthesis of diesel engine fuel is very important to increase the reaction conversion. In addition, in biodiesel production, the sustainable availability of cheaper raw materials is an important determinant of making it economically competitive with diesel oil [5,6]. Sources of triglycerides vary from edible vegetable oil such as palm oil, non-edible oil such as castor oil, and waste oil such as used palm cooking oil. The result shows that the yield of biodiesel from a mixture of used palm oil and fresh palm oil reaches 88.97 % at 120 minutes. Meanwhile, the mixture of used palm oil and castor oil reached 60.71% and used palm oil is 47.81% as shown in Figure 3.

Figure 3. The effect of different triglycerides on biodiesel yield
Due to the presence of high free fatty acid and fatty alcohol, used palm cooking oil required a higher temperature reaction in the 6-100 °C range [7,8]. Used palm cooking oil is thought to have more free fatty acids and fatty alcohol and has fewer carbonyl groups than fresh palm oil and castor oil which requires higher energy to completely break the bonds [9]. Therefore, used palm cooking oil results in the smallest biodiesel yield. The mixture of palm oil and used palm oil produces a higher yield than castor oil and used palm oil because the castor oil mixture contains a longer molecular chain, thus the yield and/or decomposition requires more time to reach the same rate as the palm oil mixture. Besides producing FAME biodiesel, it seems that this method is able to produce Greendiesel paraffin as well, Greendiesel paraffin contains paraffin chains from C14 to C20.

Table 1 shows the different raw materials that cause the formation of various types of paraffin and FAME during the reaction. The combination of used palm oil and castor oil produces most of the methyl ricinoleate. More than 88% of castor oil consists of ricinoleic fatty acids. When the synthesis process occurs, it is likely that plasma or free radicals break the C-C bonds between fatty acids.

| Table 1. Paraffin and Esters Formed by Different TGs from GC-MS Results |
|----------------------------------|-----------------|----------------|-----------------|
| TG                          | Paraffin       | Area (%)  | Methyl Ester    | Area (%)  |
| Used Palm Oil                | Heptadecane (C17H36) | 5.184     | 7,10-Octadecadienoic acid, methyl ester | 1.829     |
|                              | Pentadecane (C15H32) | 3.006     | 2. Trans-13-Octadecenoic acid, methyl ester | 0.523     |
|                              | Nonadecane (C19H40) | 2.831     |                   |           |
| Used Palm Oil and Fresh Palm Oil | Pentadecane (C15H32) | 2.243     | Hexadecanoic acid, methyl ester | 1.412     |
|                              | Heptadecane (C17H36) | 2.454     | Trans-13-Octadecenoic acid, methyl ester | 1.342     |
|                              | Nonadecane (C19H40) | 2.195     |                   |           |
| Used Palm Oil and Castor Oil  | Tetradecane (C14) | 2.103     | 11-Octadecanoic acid, Methyl ester | 2.456     |
|                              | Pentadecane (C15) | 2.173     | Methyl ricinoleate | 4.451     |
|                              | Heptadecane (C17) | 2.177     |                   |           |

3.2 Effect of CO₂ and Argon as Plasma Carrier Gas

The experiment was conducted at a temperature of 40 °C and atmospheric pressure. Argon and a mixture of argon and CO₂ (50:50% -rate) were used as a plasma carrier gas. Argon is more commonly used because it is chemically inert and it is the cheapest of all noble gases. CO₂ is chosen as a comparison because CO₂ gas is more economically efficient. Figure 4 compares the results between using argon and a mixture of argon and CO₂ as a carrier gas. The result shows that argon has a FAME yield of 53%, while the FAME yield in the mixture of CO₂ and argon is only 29.3%. Apart from the methyl ester, the mixture of argon and CO₂ contains higher methyl and alkoxy compounds than in the argon only plasma carrier gas.
Figure 4. The Effect of CO2 and Argon as Plasma Carrier Gas.

3.3 Identification of Ester by FTIR

FTIR spectroscopic analysis is used to analyze and verify the content of FAME and other compounds (paraffin and fatty alcohol) which are useful as a mixture of biodiesel. The infrared spectrum produced represents the functional groups with absorption peaks that correspond to the vibrational frequency between the atomic bonds that make up biodiesel and other compounds of paraffin and fatty alcohol. Infrared spectroscopy is a qualitative analysis of each material in the sample. On the other hand, the spectrum of palm oil and used palm oil with time variants are shown in Figure 5. The functional group of carbonyl esters in FAME can be seen in the region of wave number 1745.83 cm\(^{-1}\), the methyl functional group in the region 1377.23-1465.03 cm\(^{-1}\), and alkoxy CO ester in the area of 1030.981240.08 cm\(^{-1}\) [10]. These peaks indicate that FAME is an indication of the amount of biodiesel present in each mixture of biodiesel with petroleum because FAME shows its appearance at 1745.83 cm\(^{-1}\) and 1158.5-1456.63 cm\(^{-1}\).

Figure 5. Results of FTIR analysis for 30, 60, 90, and 120 minutes
3.4 Characterization of Produced Biodiesel

Viscosity tests were carried out on biodiesel products. The viscosity test was conducted according to ASTM D445 – 06 at bath temperature of 40 °C. The obtained data are then compared to the standard range viscosity value for biodiesel released by the Indonesian Standardization Body (SNI) SNI7182:2015 [11]. The result in Table 2 shows that the viscosity for all three biodiesels product is within the range of SNI.

| Source of Triglycerides | Viscosity test result (cSt) | Flow time (sec) | Viscosity Value based on SNI |
|-------------------------|-----------------------------|----------------|-------------------------------|
| Used palm oil           | 3.6899                      | 122.94         |                               |
| Mixture of 50:50% used palm oil and fresh palm oil | 3.7238                      | 124.07         | 2.3 – 6.0                     |
| Mixture of 50:50% used palm oil and castor oil | 3.8703                      | 128.95         |                               |

4. Conclusion

In view of the results obtained, the conclusion is as follows:

- Dielectric Barrier Discharge plasma reactor is capable of producing biodiesel from various sources of triglycerides at low temperatures, atmospheric pressure, and relatively simple sets of equipment without using a chemical catalyst, requiring very small amounts of methanol, relatively low electrical energy, and not producing glycerol as a side product.
- Biodiesel yield from a mixture of used palm oil and fresh palm oil reaches the highest result of 88.97% compared to used palm oil and mixture of used palm oil and castor, which are only 47.81% and 60.71% respectively.
- The mixture of CO2 and argon as plasma carrier gas produces 23.7% less FAME yield than argon.
- FAME characteristics exhibits its appearance at peak around 1745.83 cm\(^{-1}\), 1377.23 - 1465.03 cm\(^{-1}\), and 1030.98 - 1240.08 cm\(^{-1}\).

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