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Fatty Acid Methyl Ester Synthesis in the Cold Plasma Reactor using CO₂ and Steam Mixture

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Abstract: The synthesis of FAME (biodiesel) and alkanes (C₁₀ – C₂₀) compounds from vegetable oil and methanol in non-thermal plasma DBD reactor was performed with satisfactory results. This mainly because catalyst was not needed, relatively low energy requirement, and the absence of glycerol by-products. In addition, maximum yield of methyl ester (88.97%) was attained at an optimal reaction condition of 40 °C temperature, 1:1 molar ratio for oil to methanol, 10.2 kV plasma voltage, and a time frame of 120 minutes..

Keywords: biodiesel; dielectric barrier discharge reactor; non-thermal plasma

1. Introduction

Biodiesel or FAME (fatty acid methyl ester) is produced through conventional transesterification processes between vegetable oil and alcohol. This leads to the formation of undesirable compounds, including soap, glycerol, and free fatty acids¹, and also causes difficulties during esters separation and purification^{2,3}. This study is, therefore, aimed at investigating various process of biodiesel production, using non-thermal plasma technology. In addition, this approach has previously been implemented with promising results, due to the fact that conventional catalysts are not needed, as well as excess methanol. Furthermore, relatively low-energy is required, and glycerol is not produced as a by-product^{4,5,6}.

Non-thermal plasma, also known as cold plasma, is the electrically driven ionized gas capable of producing chemically active species, radicals or ions, such as radicals, excited atoms, molecules and ions, which acts as branched chain radicals that help in the distribution of fuel, and in conversion reactions which reduces the temperature and time needed to continue the reaction^{7,8}. The overall gas temperature in non-thermal plasma is quite close to room temperature, while high-energy electrons are in the range of 104 – 105 K⁹.

This study involves the reaction of 10%-w triglyceride solution in Pertamina DEX with methanol, using non-thermal plasma, to produce biodiesel in the Dielectric Barrier Discharge (DBD) reactor. Furthermore, the triglyceride consists of oils from fresh palm, coconut, and castor, as well as spent cooking varieties and a mixture of fresh palms and used cooking oil. Moreover, it is possible to use both edible and inedible types, and over 95% of the

world's biodiesel is presently obtained from vegetable oils¹⁰. The price competition factors, availability issues, being a characteristic source or high-priced food, make them imperfect raw materials for fuel production. Therefore, preferential use of cheaper raw materials, including crude vegetable and waste oils was considered in this investigation.¹¹.

This study investigated the effect of raw materials from different triglyceride sources, reaction temperature variations, and reaction time of biodiesel and/or other diesel engine fuels such alkanes C₁₀ – C₂₀ (paraffins) production using non-thermal plasma electro-catalysis process. This kind of synthesis process was chosen, mainly due to various corrosion problems and the design of the process encountered due to the use of catalysts in addition to being flexible and adaptive to the properties of continuous flow reactors. In this preliminary study, samples were subjected to chromatographic analysis (GC-MS and GC-FAME) just to confirm the presence of esters (biodiesel) and paraffins as a diesel fuel component. The product synthesized from this method is expected to be comparative with Indonesian National Standard for Biodiesel (SNI 7182:2015).

2. Materials and Methods

The raw materials for triglycerides are of various types. The first is used cooking oil obtained and collected from the cafeteria. Others are sources of triglycerides acquired from the domestic market, namely fresh palm oil (Tropicana® brand) and coconut oil (Barco® brand), all of which come from vegetable oil industries around Jakarta, Bekasi and Tangerang - Indonesia. As a diluent,

Pertamina DEX (fuel produced by Pertamina diesel) originating from a local gas station is utilized, while Methanol (CH_3OH) is used as a technical grade. Gases such as Argon and CO_2 are technical inert gases which act as plasma carriers. The reason for using Argon gas is because of its nature as a noble gas which can lead to non-polar reaction mechanisms, whereas CO_2 gas is expected to provide a reaction with polar mechanism on triglycerides. With the mechanism of non-polar reactions, it is expected that more alkyl radicals will be produced, while CO_2 gas is expected to have more influence on the availability of carbon sources as well as hydroxyl radical capture groups in the reaction scheme.

Fig. 1 below shows the experimental set up and design of the DBD plasma reactor.

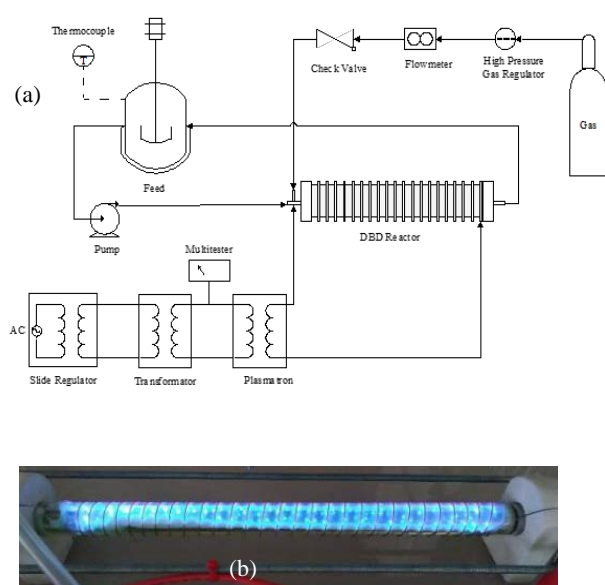


Fig. 1: (a) The experimental set up for biodiesel production using DBD non-thermal plasma reactor, (b) DBD cold plasma reactor design

A mixture of 10% triglycerides in Pertamina DEX, stored in a feed vessel was kept under stirring. A 1:1 mixture of methanol to oil ratio was heated with several temperature variations (between 40 to 60 °C), before introduction to the reactor. Therefore, the liquid feed was inserted at 1.3 mL/s, and the gas is steadily injected through the entire reaction by regulating the flow rate to 1.52 L/min, at atmospheric pressure.

The cylindrical quartz glass tube characteristic of the tubular reactor measures 18 mm in diameter, and 300 mm in length. The DBD plasma comprises of two active stainless steel SS-304 electrodes, where the outer one which is spiral-shaped and wrapped around quartz glass, serves as the low voltage. Conversely, the cylindrical variant present in the center of the tube, operates as high-voltage. Therefore a pulse effect is created by inclining the reactors' effluent part by an angle of 5 degrees.

Plasma is generated from the 1-phase voltage source, using Plasmatron, also regarded as EPT (Electronic Power Transformer). This process required the application of 10.2 kV and 30mA, also recorded at the output. Therefore, a multimeter is used to measure the electric current generated.

Tests were carried out to establish a suitable condition for the pilot and obtain better biodiesel conversion rates, by varying the residence time of samples in the reactor (from 30 to 120 minutes). This experiment was conducted with the reactor system, voltage, liquid and gas flow rate, and carrier gas held constant.

The samples were characterized by the gas chromatography analysis method, GC-FAME and GC-MS. Furthermore, the presence of various functional groups like ester, paraffins, and fatty alcohols were analyzed and verified using Fourier Transform Infrared Spectroscopy (FT-IR) analysis.

3. Results and Discussion

3.1 Effect of Temperature on Biodiesel Production

The effect of temperature on the production of biodiesel was studied, and the results are shown in Fig. 2. The reaction temperatures was varied from 40 to 60 °C, while other operating conditions were sustained, including the 1:1 molar ratio of methanol of vegetable oil, plasma voltage of 10.2 kV and constant liquid and gas flow rate. This reaction progressed for 120 minutes, and alcohol evaporation was prevented by maintaining the temperature below the methanol boiling point. Furthermore, temperature plays a crucial role in biodiesel yield, which reaches 88.97% at 40 °C, and decreases with increase in temperature. This was determined as the optimum value for this research.

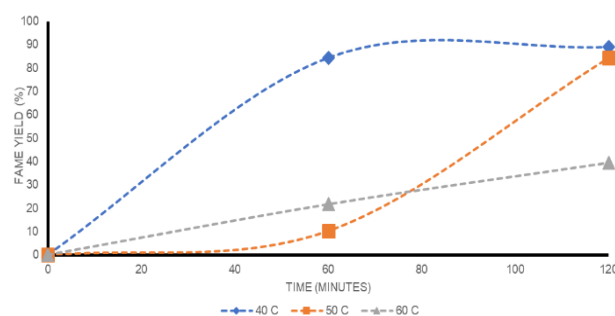


Fig. 2: Effect of Temperature on Biodiesel Production

Biodiesel conversion reactions are usually performed at low temperature, due to the ability for electric discharge formed by non-thermal plasma to provide sufficient energy needed to break chemical bonds. The use of DBD non-thermal plasma reactor might also have a significant effect because the reaction is exothermic. It utilizes C = O carbonyl bonds which are easier to decompose and

formulate fatty alcohols. Furthermore, the decrease of methyl ester yield at a higher temperature is due to the presence of chain chemical reactions resulting in the formation of other chemicals such as paraffins. The reaction should be controlled by keeping the temperature low in order to prevent excessive cracking of chemical bond¹².

3.2 Effect of Raw Materials on Biodiesel Production

This study observes the effects of different triglycerides sources used as raw materials. These were varied between edible and non-edible oils, including coconut oil (CNO), used cooking oil (UCO), a mixture of used cooking oil and fresh palm oil (MUPCO), and a mixture of used cooking oil and castor oil (MUCAO), under the maintained operating conditions.

The use of edible oils has been a major concern because of the derivation from feedstock's, and high cost. Therefore, various attempts are being made to enhance the economic viability of biodiesel, including through the adoption of non-edible oil. This is due to the available at a reasonable price¹³, and also the ability to reduce the burden of sewage treatment and water contamination¹⁴.

Furthermore, the biodiesel yield from UCO was 48% at 120 minutes. This was due to the high percentages of free fatty acids and different chemical compounds present, compared to the fresh palm oil. These comprise of dimers, polymers, and oxidized triglycerides (by hydroperoxides intermediate to obtain aldehydes, ketones, etc.). In addition, various chemical reactions, including polymerization, hydrolysis and oxidation are formed in the process, due to the presence of light, heat and oxygen¹⁵.

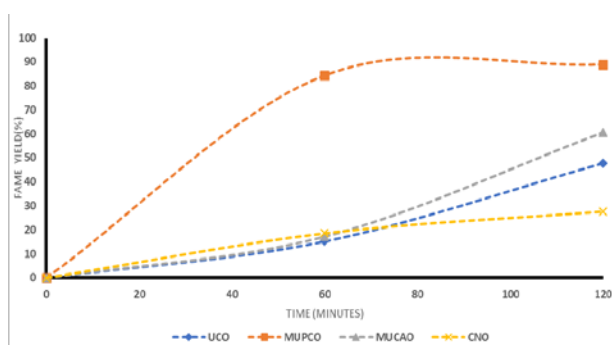


Fig. 3: Effect of Raw Materials on Biodiesel Production

However, the mixture of UCO with fresh palm oil successfully increased the methyl ester yield with a maximum yield of 89% at 120 minutes as shown in Fig. 3. The utilization of MUCAO also gives a high biodiesel yield up to 61% at 120 minutes reaction time.

3.3 Effect of Carrier Gas on Biodiesel Production

The plasma carrier gas is one of the most important factors affecting biodiesel conversion rate in DBD plasma reactor. Therefore, a mixture of argon and carbon dioxide (50:50% -rate), moistened by water vapor and a technical grade argon was used at temperature 60 °C and 10.2 kV plasma voltage.

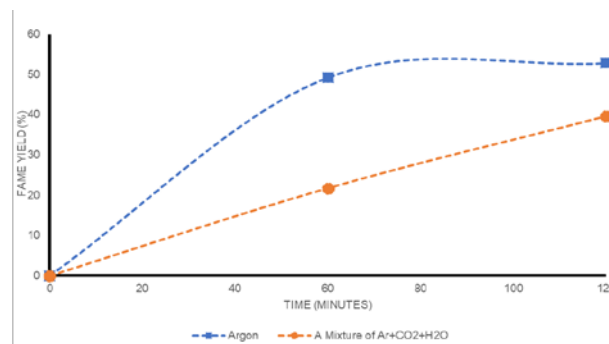


Fig. 4: Effect of Plasma Gas Carrier on Biodiesel Production

Argon is commonly used as a plasma carrier because it has a relatively low breakdown voltage¹⁶. In addition, it is an inert noble gas therefore, it does not react with reagents or experimental equipment capable of causing corrosion^{4,5}. However, the use of carbon dioxide should be considered as well since it is more economically efficient.

Fig. 4, shows that methyl ester yield from a mixture of argon and carbon dioxide as plasma carrier gas is lower than the use of argon alone. Its yield reaches 52.82% at 120 minutes reaction time while the methyl ester yield using the mixture gases only reaches 39.89%. This is because argon is more easily activated than carbon dioxide¹⁷. The plasma reaction mechanism is initiated when high energetic electrons collide with the bulk molecules of carrier gas. This process results in atom ionization, excitation and formation, alongside metastable compounds. Therefore, sufficiently high electric field leads to breakdowns, subsequently producing a large number of micro discharges. These active and metastable elements further interact with the molecules of reactants to generate methyl ester. Also, other forms of compounds have been deduced, including fatty alcohols and paraffin^{7,18}.

3.4 Characterization of Produced Biodiesel

The reaction products were analyzed using GC-MS methods, in an attempt to examine the different compounds generated during the reaction. Therefore, the respective compositions were evaluated using gas chromatography (GC), as shown in Fig. 5. The reaction between triglycerides from MUPCO and methanol in the presence of high-energetic electrons at reaction temperature of 40 °C for 120 minutes, generated methyl esters, fatty alcohols, and paraffins.

Moreover, green diesel constituents, known as paraffin

(alkane), were also produced. These include tridecane (C₁₃H₂₈), dodecane (C₁₂H₂₆), pentadecane (C₁₅H₃₂), tetradecane (C₁₄H₃₀), and hexadecane (C₁₆H₃₄), heptadecane (C₁₇H₃₆), nonadecane (C₁₉H₄₀), and eicosane (C₂₀H₄₂). There are no glycerol compounds formed during the reaction. Non-thermal plasma is expected to be able to break the chemical bonds of glycerol resulting in radicals such as CH₃•, H•, CH₃O• which further reacts with triglycerides resulting in methyl ester and alkanes.

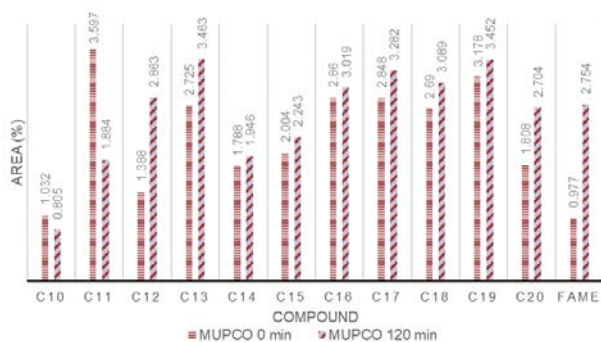


Fig. 5: Identification and composition of GGC-MS chromatogram at respected reaction time

Density is an important principal fuel property, used to estimate the quantity of sample to be injected for adequate combustion^{19,20}. Table 1 shows an illustration and comparison of the values obtained against the Indonesian National Standard for Biodiesel (SNI 7182:2015)²¹. Furthermore, viscosity is a measure of fuel flow ability²⁰. This parameter also plays a major role in spray atomization, as well as penetration²², and 10–15 folds higher values were recorded for biodiesel compared to conventional fossil varieties. Hence, there is a higher propensity for reduced thermal efficiency, insufficient atomization and soot deposit intensification^{14,15, 23,24}. The tests for viscosity were performed according to the ASTM D445 – 06²⁵.

Table 1. Properties of Biodiesel Obtained Compared with Biodiesel Standard

Biodiesel Properties	Raw Materials	Values obtained from current study	SNI 7182:2015
Density (g/cm ³)	UCO	0.827	0.85 – 0.89
	MUPCO	0.856	
	MUCAO	0.826	
Viscosity at 40 °C (mm ² /s)	UCO	3.764	2.3 - 6.0
	MUPCO	3.724	
	MUCAO	3.844	

Table 1 shows the kinematic viscosity of biodiesels produced from different triglycerides sources. The biodiesel derived from MUCAO demonstrated maximum viscosity of 3.84 mm²/s, which was out of range, while MUPCO was minimal, at 3.72 mm²/s.

Summary

This study analyzes the possibility to produce biodiesel from used cooking oil using dielectric barrier discharge non-thermal plasma reactor. A major advantage of this process is that methyl ester can be obtained in the absence of chemical catalysts and without the formation of unwanted co-product such as glycerin and soap. The reaction is able to proceed at low temperature and electrical energy. The biodiesel conversion decreases with increase in temperature. It was found that biodiesel production from the mixture of palm oil and used cooking oil was optimized at a reaction temperature of 40 °C, a plasma voltage of 10.2 V, oil-to-methanol molar ratio of 1:1, and 120 minutes reaction time resulting in maximum biodiesel yield of 88.97%.

Acknowledgements

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