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The Effect of Plasma Electrolysis for Biodiesel Synthesis Using Waste Cooking Oil as a Raw Material and KOH Catalyst

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A B S T R A C T

Indonesia's high cooking oil consumption is directly proportional to the production of used cooking oil waste that can pollute the environment. Waste cooking oil can be used as raw material for biodiesel using the plasma electrolysis method. Plasma electrolysis is a synthesis process that applies a high voltage to the process system. This study aims to determine the effect of the plasma electrolysis method with variations in voltage (400 - 500 volts) and the type of reagent (Methanol and ethanol) on the yield and characteristics of biodiesel. The process is carried out by reacting waste cooking oil with a reagent given voltage until an electric discharge occurs. Two layers are formed, and the specific energy requirements for the synthesis process are calculated. The results show that a voltage of 500 volts with methanol reagent produces a yield of 85.73%-w with characteristics according to the SNI 7128:2015 standard such as density 888.36 kg/m3, viscosity 5.79 Cst, acid number 0.39 mg - KOH/g, fatty acid methyl ester (FAME) content 97.56% and flash point 117oC and with a specific energy of 1758,031 J/mL.

INTRODUCTION

The liquid form of fuel is consciously researched upon as only few alternatives are available in solid and gaseous fuel category to compete with them [1]. Biodiesel is chemically a methyl ester from Fatty Acid Methyl Ester (FAME) resulting from the transesterification process, which generally has better combustion quality than fossil-based diesel which is characterized by a higher cetane value of biodiesel (45 – 65) than fossil diesel (40 – 55) [2]. According to recent life cycle assessment studies, the emissions of CO_2 and CO can be reduced by 8-41% by using biodiesel. Biodiesel is sulfur free, non-toxic, and biodegradable, with much more lubrication capability compared to petroleum diesel [3].

In Indonesia, the biodiesel industry shows an increase in quantity and capacity. Biodiesel production is consumed on the domestic market to be blended with diesel fuel as mandated by the government and for export purposes. The installed capacity of the biodiesel industry in Indonesia has reached 18,1 million kilolitres (kL). In February 2023, a progressive policy introduced the use of B35, a mixture of 35% biodiesel and 65% diesel fuel, which confirms Indonesia as a leading country in terms of biodiesel utilization [4]. This shows that biodiesel is still a research topic that continues to be developed.

The significant volume of biodiesel is produced from food-grade oils such as edible vegetables and soybean oils via transesterification, which creates a competition between food supply for human consumption and biodiesel production [5]. Based on data from the United States Department of Agriculture (USDA), in 2019, domestic consumption of palm oil reached 12.75 million tons, directly proportional to waste cooking oil production in Indonesia, reaching 4.000.000 tons/year [6]. The existence of waste cooking oil pollutes the environment. Waste cooking oil has a high fatty acid content, making it possible for biodiesel production to be processed from this raw material source [6]. Apart from that, the advantages that make waste cooking oil have the potential to be used as fuel are that the energy content is quite large and has a high heat potential. Also, waste cooking oil is not easy to ignite, so it is safe, and in terms of storage, there are no special procedures or requirements [7].

Much research has been carried out regarding biodiesel. For example, the synthesis of biodiesel from vegetable oils using conventional methods such as alcohol and base catalysts, biodiesel synthesis using solid catalysts, and recently, the plasma method. Conventional biodiesel synthesis usually uses an excess of methanol (molar ratio oil to methanol 1:6) and 1%-weight of KOH as a base catalyst at 60°C for 3 hours, obtaining conversion 98,5% [8]. Synthesis of biodiesel by waste cooking oil and solid base catalyst 0.5%-weight NaOH/Chitosan-Fe_3O_4, methanol to oil ratio 6:1 for 4.5 hours at 25°C obtained biodiesel yield 92% [9]. Recently, biodiesel synthesis from oleic acid by liquid phase plasma discharge with a weight ratio of H_2SO_4 to oleic acid 2.38% and methanol to oleic acid molar ratio of 0.08 in 4 minutes treatment resulted in 80.78% reaction conversion [5].

Plasma is an ionized gas with high-energy electrons, free radicals, chemically active ions, and excited states. Advanced methods such as microwaves, ultrasound, and plasma can significantly reduce the reaction time and improve product yields in biodiesel synthesis. In biodiesel production, plasma has been investigated to initiate low-temperature transesterification. In a plasma-assisted catalytic system, the plasma could activate the reactions directly. The interaction of plasma with the catalyst provides a synergistic effect, where the plasma improves the activity of the catalyst, and the catalyst enhances the impact of the plasma [10].

A type of plasma, a liquid-phase plasma discharge reactor, was successfully applied to convert soybean oil into biodiesel because the non-thermal plasma technology could produce the combined effect of microwave and ultrasound techniques [5]. The plasma electrolysis method (Contact Glow Discharge Electrolysis) is a development of conventional electrolysis where the plasma electrolysis process will form an electric discharge in the electrolyte solution due to the high voltage used, which causes differences in electric charge [11]. In biodiesel synthesis using the plasma electrolysis method, the first stage is to produce a tetrahedral intermediate from nucleophilic attack, the second stage is the process of forming alkyl esters and diglyceride anion compounds, and the last stage is the regeneration of the active species, which will later react from the second molecule of alcohol and is followed by catalyst recovery base [12].

The plasma formed in plasma electrolysis is expected to be in the cathode area because the specific energy consumption in the cathodic plasma process is lower (729 J/mL) compared to the specific energy consumption in the anodic plasma process (910 J/mL) [12]. This research uses the plasma electrolysis method with waste cooking oil as raw material accompanied by voltage variations and reagent methanol and ethanol to improve the reaction time of biodiesel synthesis and reaction temperature, which can produce high biodiesel yields and is economical in terms of energy consumption.

METHODS

Material and Apparatus

The materials used in this research were waste cooking oil obtained from a fast-food chicken restaurant, 96% purity technical grade methanol, 96% purity technical grade ethanol. KOH and phenolphthalein indicator are form Merck Chemical.

The equipment used includes a 400 mL borosilicate beaker, tungsten electrodes and SS316 stainless steel, power supply, multimeter, separating funnel, cables, clamps, oven, pycnometer, NDJ-5S, viscometer, magnetic stirrer. GC-MS analyzed biodiesel products.

Pretreatment Process and Characterization of Used Cooking Oil

1.5 L of waste cooking oil from fast food restaurants was filtered using filter paper to remove solids impurities from frying. The waste cooking oil characterization process was carried out to determine the density using a pycnometer, viscosity using an NDJ-5S viscometer, acid number, and %FFA using the titration method using KOH 0.1 N, and water content using the oven heating method. The most critical data is %FFA because it determines the following process that will be carried out. If %FFA is > 2%, the process must first be done by esterification with a 98% H_2SO_4 acid catalyst. If <2%, the process can be carried out directly by plasma electrolysis with a KOH catalyst.

Set of apparatus

The biodiesel synthesis apparatus using plasma electrolysis is prepared and presented in Figure 1.

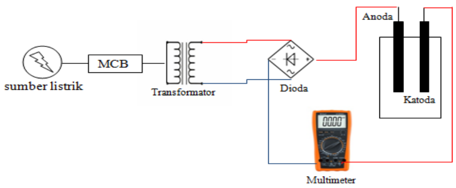

Figure 1. Biodiesel synthesis apparatuses schematic

Characterization of Plasma Formation

Plasma formation characterization was carried out to obtain a transition from conventional electrolysis to VB (Breakdown Voltage) plasma electrolysis. The operating conditions for the first plasma formation VD (midpoint voltage) in methanol and ethanol reagents will be used as a reference for biodiesel synthesis. The voltage in biodiesel synthesis was varied above the VD to determine its effect on the yield and characteristics of the biodiesel formed.

Biodiesel Synthesis Using Plasma Electrolysis

The primary process, namely the synthesis of waste cooking oil into biodiesel using plasma electrolysis, is carried out by varying the operating voltage of 400 volts, 450 volts, and 500 volts and the use of alcohol (methanol and ethanol) to obtain optimum yield of the biodiesel formed. The molar ratio of oil to methanol or ethanol is 1:24, and KOH catalyst is 1%-weight. Transesterification using plasma electrolysis occurred from the room until it reached a specific temperature for 30 minutes.

Biodiesel Purification

The crude biodiesel is separated from glycerol as a side product using a separating funnel for around one day. Then, washing is carried out to remove the remaining alcohol still involved in the biodiesel. The final stage of purification is heating crude biodiesel in the oven at 105°C for 2 hours to evaporate the water content still contained in the biodiesel due to washing.

Biodiesel Analysis

The biodiesel resulting from the research was then analyzed: acid number, density, viscosity, water content, ester content, and flash point. This value is compared with the SNI 7128:2015 standard and the specific energy requirements of the synthesis process.

RESULT AND DISCUSSION

Characterization of Waste Cooking Oil

The results of waste cooking oil characterization are shown in Table 1.

Table 1. Waste Cooking Oil characterization

No	Parameter	Unit	Value
1	Acid value	Mg KOH/g	1,038
2	Density	Kg/m^3	966
3	viscosity	cst	12,42
4	Water content	%-w	0,22
5	FFA	%	0,474

The %FFA content of waste cooking oil was below 2%, so the biodiesel synthesis can be done directly using a KOH catalyst's plasma electrolysis method.

Characteristics of Plasma Formation

The process of characterizing plasma formation using methanol and ethanol reagents is shown in Figures 2 and 3, respectively.

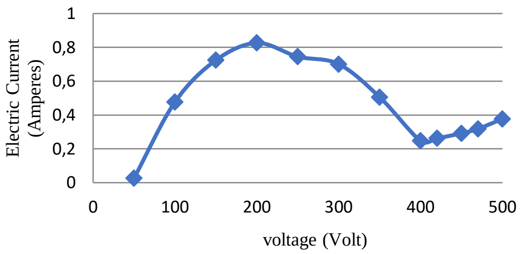

Figure 2. Characteristics of Plasma Formation in Waste Cooking Oil + KOH + methanol

In Figure 2, it can be seen that the VB (breakdown voltage) value is at a voltage of 200 volts with an electric current of 0.826 amperes, and the voltage value for the first plasma formation (midpoint voltage) is 400 volts with an electric current of 0.247 amperes.

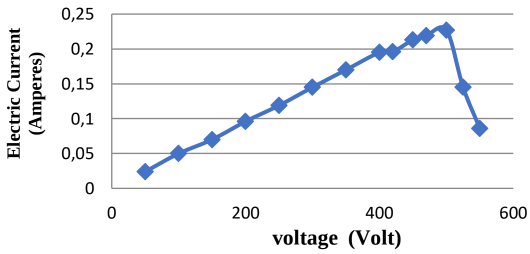

Figure 3. Characteristics of Plasma Formation in Waste Cooking Oil + KOH + Ethanol

In Figure 3, the voltage required to reach the VB (Breakdown Voltage) point for ethanol reagent is greater than that of methanol reagent, namely 500 volts with an electric current of 0.227 amperes. At the same time, the VD (Mid-Point Voltage) value has not yet been established at the maximum voltage. Plasma can still form if a greater voltage is applied because there has been a decrease in electric current at more than 500 volts. This decrease indicates that gas bubbles have formed and split, which will continue with the Joule heating effect, and plasma is formed.

Biodiesel Synthesis

In biodiesel synthesis, bubbles formed in the cathode (tungsten) area at 50 – 100 volts. Meanwhile, bubbles formed and broke due to the Joule heating effect when the voltage rises to 200 – 300 volts. At a voltage > 400 volts, plasma sparks begin to form, and evaporation of the electrolyte solution is speedy, marked by the presence of white fog around the reactor. The phenomenon during biodiesel synthesis is shown in Figure 4.

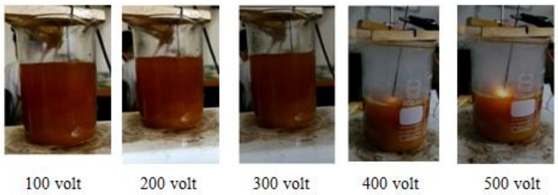

Figure 4. The phenomenon during biodiesel synthesis

Biodiesel Purification

The biodiesel is purified in a separating funnel for one day until two layers are formed. The top layer is crude biodiesel, and the bottom is glycerol, as shown in Figure 5. (1). In Figure 5. (2) Biodiesel was washed thrice using hot water to remove residual impurities. Next, the crude biodiesel is heated in the oven for 2 hours at a temperature of 105°C to evaporate the water until biodiesel is obtained, as shown in Figure 5. (3).

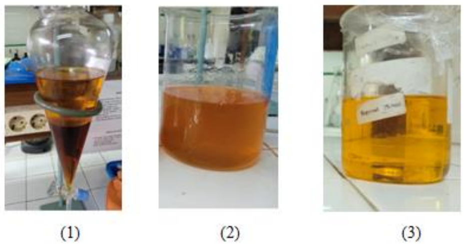

Figure 5. Biodiesel Purification

Effect of Voltage and Solvent on Biodiesel Yield

Figure 6 shows the effect of voltage on biodiesel synthesis with methanol solvent; the greater the voltage applied, the greater the yield of biodiesel formed. This phenomenon is due to increasingly large radical species creating and combining with radical hydrogen [13]. The collision of energetic electrons generated by plasma with reactants will be reacted with free radicals and chemical species, including ions [14]. The more significant the energetic electron obtained from voltage, the more waste cooking oil is converted into biodiesel.

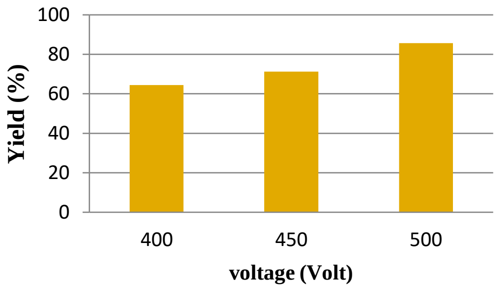

Figure 6. The Effect of Voltage on the yield of Biodiesel Synthesis using Methanol Solvent

The synthesis of waste cooking oil did not form biodiesel in ethanol solvent even though it was carried out for more than 1 hour. The result is shown in Figure 7.

Figure 7. Synthesis of Biodiesel with Ethanol Solvent

In Figure 7, two layers of product are formed. The top part is soluble in water, while the bottom is not. This result is because ethanol has a longer carbon chain than methanol, so the reactivity of ethanol is lower. This trait caused the biodiesel synthesis using ethanol solvent did not occur ideally. The biodiesel synthesis using methanol solvent with the yield according to Figure 6 requires specific energy, as shown in Figure 8.

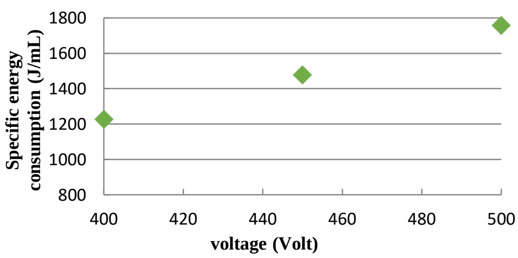

Figure 8. Specific energy consumption in biodiesel synthesis using methanol solvent

Figure 8 shows that the greater the voltage, the greater the specific energy required. Apart from that, the length of the cathode immersed, which is as deep as 3 cm, also affects the needed specific energy. Based on theory, the deeper the cathode is immersed, the greater the specific energy requirement. The reacting factors in producing hydrogen radicals also influence the energy needed. The more hydrogen radicals are created and combined with the excited secondary electrons, the lower the electric current flows. It can produce plasma optimally, and the energy required is smaller [15].

Biodiesel Analysis

Biodiesel characterization was compared with SNI 7128:2015 standards with the following results:

a) Density, Viscosity and Acid Number

Tables 2-4 show that the density, viscosity, and acid number of biodiesel formed complies with SNI 7128:2015 standards. The decrease in viscosity in biodiesel is due to breaking the carbon chain in fatty acids and fewer double bonds (Sinaga et al., 2014). Biodiesel acid numbers that comply with SNI indicate that the fatty acids in waste cooking oil have been converted into FAME biodiesel.

Table 2. Density of biodiesel from waste cooking oil synthesis with methanol solvent

Voltage (volt)	Density (kg/m^3)	Standard density (SNI 7128:2015)
400	888.76	
450	890.26	850-890
500	888.36	

Table 3. Viscosity of biodiesel from waste cooking oil synthesis with methanol solvent

Voltage (volt)	viscosity (kg/m^3)	Standard viscosity (SNI 7128:2015)
400	6.05	
450	5.79	2.3-6
500	5.71	

Table 4. Viscosity of biodiesel from waste cooking oil synthesis with methanol solvent

Voltage (volt)	Acid value (mg KOH/g)	Standard Acid value (SNI 7128:2015)
400	6.05	
450	5.79	Max 0.5
500	5.71	

b) Water content

Table 5 shows the water content value of biodiesel still does not meet the SNI 7128:2015 standard. This value is due to the less-than-optimal heating process after washing the biodiesel. Another factor is the reaction of the KOH catalyst with air to increase the water content.

Table 5. Water content of biodiesel from waste cooking oil synthesis with methanol solvent

Voltage (volt)	Water content (%-w)	Standard Acid value (SNI 7128:2015)
400	0.471	
450	0.424	Max 0.05
500	0.373	

c) FAME composition

The FAME composition of biodiesel from the synthesis of waste cooking oil with methanol solvent at a voltage of 500 V is 97.56% area, as shown in Figure 9. The highest FAME constituents are methyl oleate (43.36% area) and methyl palmitate (34.99% area).

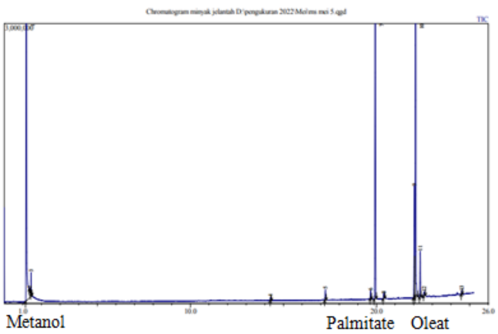

Figure 9. GCMS of biodiesel from synthesis of waste cooking oil with methanol solvent at a voltage of 500 V

The FAME composition of biodiesel from the synthesis of waste cooking oil with methanol solvent at a voltage of 500 V is shown in Table 6.

Table 6. Composition of biodiesel from waste cooking oil synthesis with methanol solvent

No.	Component	Amount (%-area)
1	Methyl laurate	0.3
2	Methyl myristate	1.01
3	Methyl palmitoleate	0.78
4	Methyl linoleate	12.15
5	Methyl palmitate	34.99
6	Methyl oleate	43.36
7	Methyl stearate	4.5
8	etc	0.46

d) Flash point

The flash point of biodiesel from the synthesis of waste cooking oil with methanol solvent at a voltage of 500 V follows SNI 7128:2015 standards, as shown in Table 7.

Table 7. Viscosity of biodiesel from waste cooking oil synthesis with methanol solvent

Voltage (volt)	Flash point (°C)	Standard Flash point (SNI 7128:2015)
500	117	Min.100

CONCLUSION

The synthesis of biodiesel from waste cooking oil using methanol solvent and the plasma electrolysis method has been successfully carried out. The research results show that the greater the electrical voltage applied to the mixture of waste cooking oil with methanol solvent, the higher the biodiesel yield. At 400 volts, 450 volts, and 500 volts, the yields are 64.44%, 71.22%, and 85%, respectively. Meanwhile, specific energy shows that the higher the voltage applied during the plasma electrolysis process, the greater the energy consumption required when the cathode is immersed as deep as 3 cm.

The results of biodiesel analysis consisting of density, viscosity, acid number, ester content, and flash point have met SNI 7128:2015 standards. In biodiesel synthesis using ethanol solvent, plasma has not yet been formed, so biodiesel is not included.

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