

Dielectric barrier discharge plasma application to convert used cooking oil into biodiesel

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Abstract. Plasma research on used oil (waste cooking oil) processing into biodiesel using Dielectric Barrier Discharge (DBD) has been conducted. Plasma technology can process used oil into biodiesel without using chemical catalysts. The DBD reactor in this research was formed by inside electrode, barrier and outside electrode components. The inside electrode is screw stainless steel with diameter 0,79 cm. The barrier is pyrex tube with thickness 0,25 cm. The outside electrode is copper wire which is wound into the pyrex tube. Plasma was flowed by argon gas with debit rate 2 L/minutes. In plasma reactor was connected AC voltage 1,6 kV. The oil mixed with methanol by volume ratio 6:1. Both materials were inserted into a reactor with the time variation of 30, 60, 90, 120, 150 min. The optimum result was obtained at 30 minutes treatment. The oil which was resulted has density 0.87 g/cm³, viscosity 4.1 mm²/s, acid number 0.56 mg KOH/g, iodine number 31.64% -mass and 16.01% are mono-alkyl ester compound, and it was classified in National Indonesian Standard (NIS).

1. Introduction

Utilization of plasma to treat oil waste has been done [1,2] Plasma generation can be carried out by gas flowing on two electrodes connected by a high voltage source. In both electrodes there will be electric discharges which can ionize the gas through it [3]. One of the techniques of plasma generation is the discharge of dielectric barrier or Dielectric Barrier Discharge (DBD) [4,5]. The characteristic of DBD plasma has a narrow discharge gap with millimeter distance and one of its electrodes is coated by the insulator. DBD's application on the environment has been carried out among others for the production of biodiesel from fatty acids from food industry waste [5] for upgrading heavy oil in a conventional thermal cracking system under atmospheric pressure [2], for biodiesel production from vegetable oil over plasma reactor [6]. There are some researches for POME treatment by using non thermal plasma. Treatment of POME by a combined sand filtration-DBD system for preliminary study has been done [7].

2. Methods

Figure 1 shows the experimental set up of this research. Dielectric Barrier Discharge Plasma was constructed by an active electrode that was made of stainless steel screw with a diameter of 8 mm, Pyrex



pipe with a diameter of 20 mm and an outer diameter of 22.5 mm as barrier and the outer electrode was made of copper wire with a diameter of 1.83 mm and its wrapped around the pipe as much as 30 windings. This DBDP was generated by AC high voltage. Electrical parameters of DBDP determined through a voltage divider (HV Probe DC Voltage DC max 40 kV; 28 kV AC EC code number 1010, En G1010). Electrical signal from the probe detected by an Oscilloscope GOS-653, 50 MHz. charge carriers.

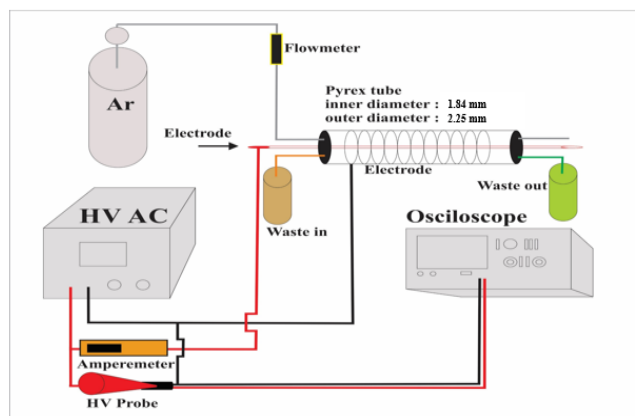


Figure 1. Experimental set up.

The electric current, that was generated in the reactor was measured by using a multimeter (Sunwa TRXn 360) and ammeters (Kyoritsu, AC/DC digital Clamp meter). Argon gas as the industrial gas (Ar, 99.95%) was inserted into the reactor by regulating the gas flow rate in the range of 1-10 L/min. Voltage and electronic signals are generated can be observed using an oscilloscope. Gas flow rate was measured using a flow meter (Koploc Kojima Model RK 1600 R). Pome together with argon gas introduced into the DBD reactor. Plasma generated in the reactor. Capacitive current measured as an average current of discharge. The Dielectric Barrier Discharge plasma assembly consists of an inner electrode made of stainless steel with a diameter of 0.81 cm and a height of 50 cm and an outer electrode made of copper wire windings of 0.12 cm in diameter. Both electrodes are blocked by a barrier made of tubular pyrex with a thickness of 0.3 cm and a height of 42 cm. Both of these electrodes are connected to a high-voltage AC source, and are also connected to the amperemeter and HV probe. The oil is put into the reactor and treated with plasma with no flow in the pyrex.

The mobility of charge carriers in each plasma reactor can be determined by an I-V characteristics. It has to harmonize of Robinson's formula with our experimental condition where there are three types of dielectric materials between two electrodes. Robinson's formula [8] must be modified, and the relationship between I_s (V) follow [7]:

$$I_s = \frac{2\mu_{RT}\epsilon_i S}{d^3} (V - V_i)^2 \quad (1)$$

Where S is a surface area of passive electrode in cm^2 and d is the distance between the electrodes in cm. Into the space between the electrodes inserted dielectric materials eg air/gas, liquid and solid, with each of the dielectric permittivity is ϵ_1 for material 1, ϵ_2 for material 2, and ϵ_3 for material 3. Furthermore, ϵ_i is an effective permittivity for 3 dielectric materials. By using the formula (2) average mobility μ_{RT} of charge carriers can be determined. The mono-alkyl ester component present in the bioisel can be determined using GC-MS. GS-MS stands for Gas Chromatography-Mass Spectrometry. GC-MS is a method of separating organic compounds using two methods of compound analysis ie gas chromatography (GC) to analyze quantitative quantity of compounds and mass spectroscopy (MS) to analyze the molecular structure of the analyte. Gas chromatography is one of the spectroscopic techniques that uses the principle of separation of the mix based on the difference of migration speed of its constituent components [9].

3. Results and discussion

The mobility of the charge carriers can be determined using equation (1). By using the value of the gradient of the linear graph the relationship \sqrt{I} as a function of V average mobility can be found. Figure 3 shows the charge carrier particles mobilities as the function of gas flow rate in present of samples and without a sample. The charge carrier particles, in this case, are positive ions, negative ions, electrons, in electric field would move with the average speed. The magnitude of the drift velocity is proportional to the magnitude of the electric field and the value of mobility. Mobility is defined as the freedom of the particles to move, either in random motion [7]. The mobility of charged particles in the presence of samples (methanol and waste oil) is always greater than the mobility of charge carriers without samples. In other words, only the argon plasma occurs inside the reactor. This phenomena supports our finding that waste oil has transformed into lighter compounds and become biodiesel. Plasma formed inside reactor (sample and argon gas) produce more charged compounds and magnify electrical current.



Figure 2. Photographs plasma in DBD reactors, plasma argon with oil sample.

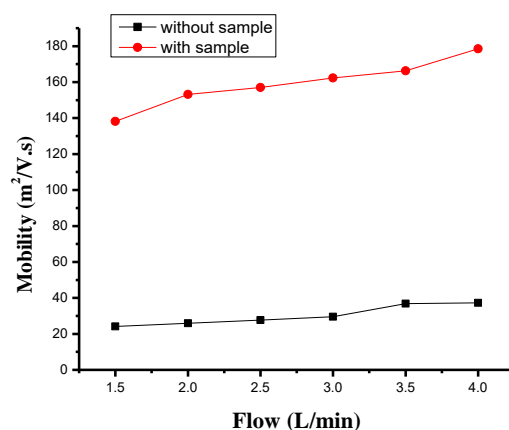


Figure 3. Average mobility as a function of gas flowrate, without sample and with sample [7].

Figure 4 shows photograph of waste oil and waste oil after treatment. Indicator treated waste samples depends on treatment time (tt), Samples A (tt = 30 minutes), B (tt=60 minutes), C (tt= 90 minutes), D (tt=120 minutes) and E (tt=150 minutes). According to color of oil treatment, after 30 minutes treatment, we found that the color is more clear compare with control.

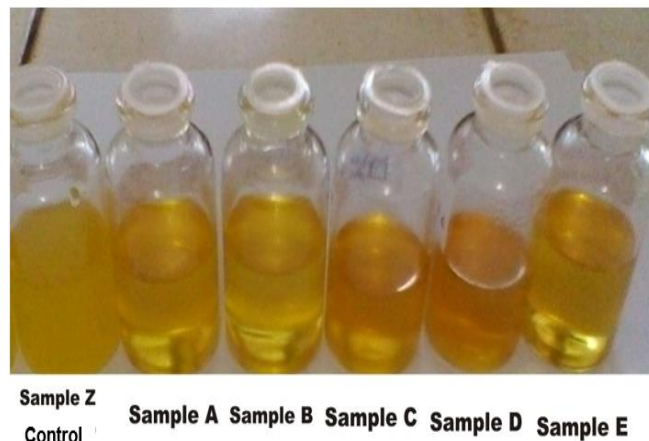


Figure 4. Samples of waste oil treatment depend on time treatment (tt).

The oil was mixed with methanol and fed by argon gas with a flow rate of 2 L / min during treatment. The resulting plasma was a substitute for chemical catalysts in conventional biodiesel producing. Furthermore, plasma technology will produce biodiesel from cooking oil without having to use chemical catalyst.

The results we obtained from this study, similar to those obtained by Cubas et al. [10]. Biodiesel can be produced from cooking oil by using DBD type corona reactor using 17 kV AC voltage and argon gas with flowrate of 1 l / min.

3.1. Parameter biodisel quality

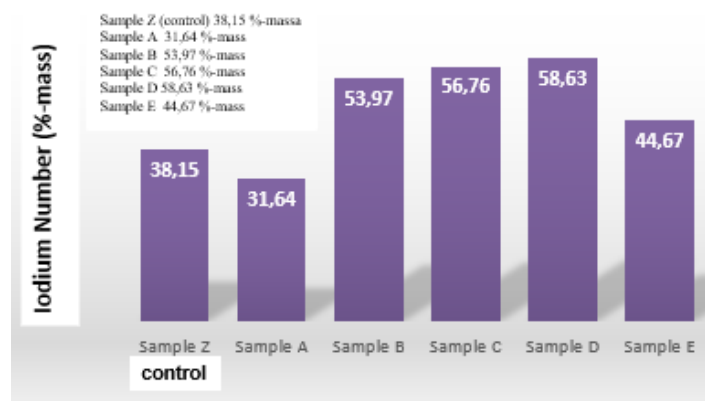


Figure 5. Iodine number for several samples with difference time treatments.

Viscosity is an important parameter in determining the quality of biodiesel. Viscosity will affect the process of spraying and combustion of fuel in diesel engines. High biodiesel viscosity is very good to help lubrication machine but will complicate the process of atomization. The kinematic viscosity is related to the fatty acid composition of the raw material, the amount of the double bond, and the purity of the final product. The kinematic viscosity is directly proportional to the length of the carbon chain and inversely proportional to the number of double bonds. The longer the carbon chain of fatty acids and alcohol the greater the viscosity. Conversely, the viscosity is higher if the oil gets saturated [11]. Another factor that also influences is the storage process. The oxidation reaction will increase the viscosity of biodiesel [12]. The kinematic viscosity for biodiesel in this study was analyzed at 40°C. [13].

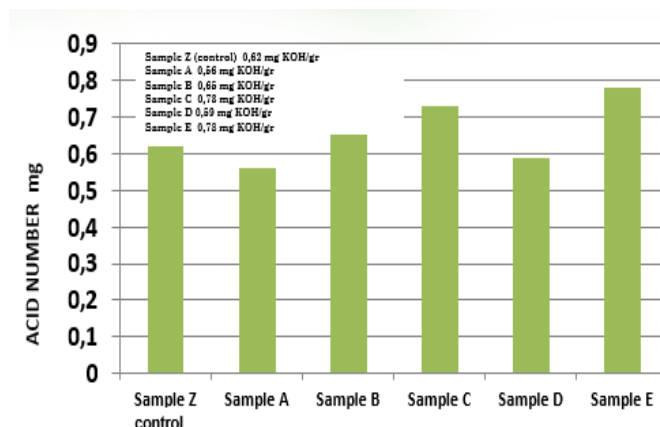


Figure 6. Acid number for several time treatment.

The oil mixed with methanol by volume ratio 6:1. Both materials were inserted into a reactor with the time variation of 0, 30, 60, 90, 120, 150 min. The optimum result was obtained at 30 minutes treatment. The oil which was resulted has density 0.87 g/cm^3 , viscosity $4.1 \text{ mm}^2/\text{s}$, acid number 0.56 mg KOH/g , iodine number 31.64% -mass and 16.01% are mono-alkyl ester compound table 1. By using GC-MS test we know the compounds contained in the sample after treatment. The samples tested in this study were A sample with time treatment of 30 minutes. This sample has been used cause of 4 parameters including acid number, iodine number, density and viscosity, sample A has smaller than control. Based on the results of GC-MS test, the mono-alkyl ester content is presented in table 1.

Table 1. Mono-alkyl ester compound and its concentration

Name	Concentration(%)
Propoanic acid 1-(acetyloxy)-, 5 methyl-2-(1-methylethyl) cyclohexyl rster (CAS)	0,38
Hecadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)	11,30
Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)	1,64
9- Octadecanoic acid (Z)-,9-octadecentyl ester, (Z)-(CAS)	0,62
2-[5-(2-Hidroxy-propyl)-tetrahydrofuran-2-yl]-propionic acid, t-butyl ester	0,38
Decanoic acid, octadecyl ester (CAS)	1,24
Undecanoic acid, 11-bromo-, undecyl ester	0,22
Hecadecanoic acid, 3-[(trimethylsilyl)oxy]propyl ester (CAS)	0,23
Total Concentration	16,01

We found concentration of mono-alkyl ester by using GC analysis. Figure 6 shows the overall peaks of GC-MS test results in sample A with a treatment time of 30 minutes. The Willey Library may be used as a reference to the GC-MS test to confirm whether the peak is standardized (based on both reviewer's time and detail structure) to identify peaks present in the sample using high probability (review time, detail structure).

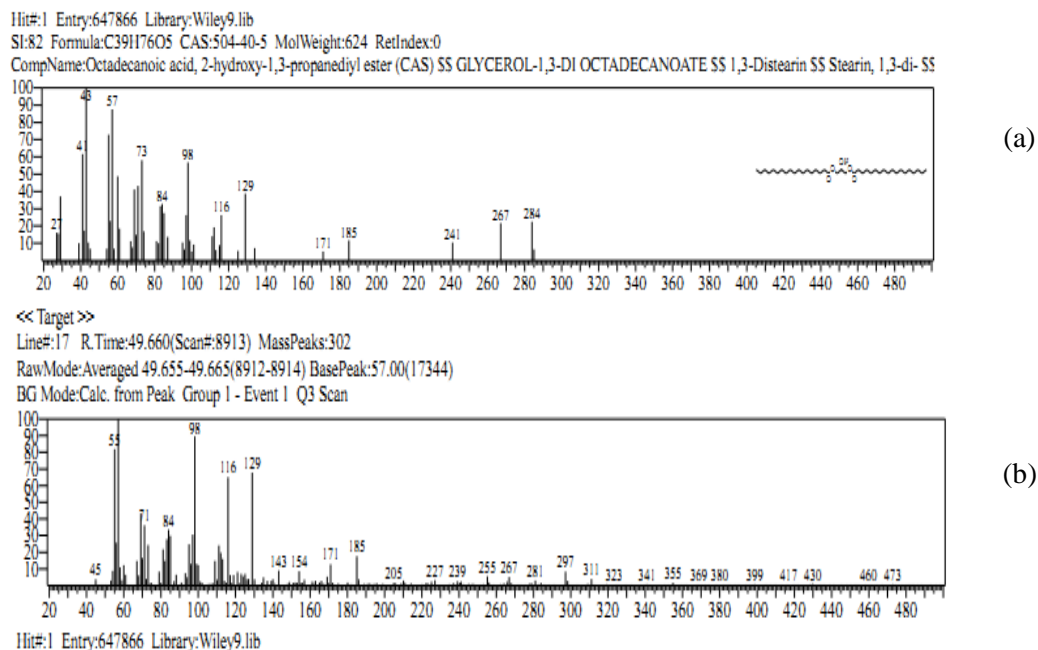


Figure 7. (a) Peak Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester of our biodiesel.
 (b) Peak Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester from Willey Library.

Figure 7 (a) shows the peak of Hecadecanoic acid, 2-hydroxy-1,3-propanediyl ester test results, while figure 7 (b) shows peak of Hecadecanoic acid, 2-hydroxy-1,3-propanediyl ester of reference Willey Library. Figure 7 (a) shows the peak of Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester test result, while figure 7 (b) indicates peak Octadecanoic acid, 2-hydroxy-1,3-propanediyl ester of Willey Library.

4. Conclusion

Based on the research that has been done can be concluded several things including: The electric current generated in the reactor without and with the sample increases with the increase of voltage. Mobilities of charge carriers with sample inside ther DBD reactor always greater than mobilities charge carries without samples. The most effective time for the manufacture of biodiesel by using a spiraling plasma dielectric barrier Discharge using a voltage of 1.6 kV and argon discharge of 2 L / min is 30 minutes, since the final sample produced has an acid number, iodine, the density value and the viscosity value are smaller than the control variables. There are 16.01% of mono-alkyl ester compounds produced in this study, so the Dielectric Barrier Discharge spiral-screw plasma can potentially process waste oil (cooking oil) into biodiesel.

References

- [1] Honorato Hercilio, Renzo C Silvia, Cleiton K Piumbini, Carlos G Zucolotto, Andre A De Souza, Alfredo G Cunha, Francisco G Emmerich, Valdemar Lacerda Jr and Eustaquio V R de Castro 2011 *Fuel* **92**(62)
- [2] Hao Haigang, Bao S Wu, Jianli Yang, Qiang Guo, Yong Yang and Yong W Li 2014 *Journal Fuel* **149**:162
- [3] Fridman Alexander 2008 *Cambridge University Press*.
- [4] Harry John Ernest, Wiley VCH Verlag GmbH and Co KGaA 2010 Weinheim
- [5] Jahanmiri A, M R Rahimpour, M Mohamadzadeh Shirazi, N Hooshmand and H Tanghvaei 2012 *Chemical Engineering Journal* **191**: 416
- [6] Istadi, Didi Dwi Anggoro, Puput Marwoto, Suherman and Bambang Tri Nugroho 2009 *B. Chem. React. Eng, Catal.* **4**(1) 23

- [7] Muhammad Nur, Yovita Asri Ameliaa, Fajar Arianto, Andi Wibowo Kinandana, Intan Zahar, Ade Ika Susan and Jujur Pratama 2017 *Procedia Engineering* **170**(325)
- [8] Robinson M 1961 Movement of air in the electric “wind” of the corona discharge *AIEE Trans.* 80 143
- [9] Pavia Donald L, Garry M Lampman, George S Kritz and Randall G Engel 2006 *Introduction to Organic Laboratory Techniques (4th Ed)* (Thomson Books Cole) 797-817
- [10] Cubas A LV, M M Machado, C R S C Pinto, E H S Moecke and A R A Dutra 2015 *Journal Waste Management*
- [11] Höllig A, Schug A, Fahlenkamp A, Rossaint R and Coburn M 2014 *International Journal of Molecular Sciences* 15 1817
- [12] Gerpen J V and G Knothe 2005 *The Biodiesel Handbook* (Champaign Illinois: AOCS PRESS)
- [13] Canakci M and Gerpen J Van 1999 *J. Transactions of the ASAE* 42(5):1203