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Research Article

Electro-Catalysis System for Biodiesel Synthesis from Palm Oil over Dielectric-Barrier Discharge Plasma Reactor

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Abstract

Biodiesel synthesis reaction routes from palm oil using plasma electro-catalysis process over Dielectric-Barrier Discharge (DBD) plasma reactor were studied. The study was focused on finding possible reaction mechanism route during plasma electro-catalysis process. The prediction was performed based on the changes of Gas Chromatography Mass Spectrometer (GC-MS) and Fourier Transform Infra Red (FT-IR) analyses to the biodiesel products with respect to time length of plasma treatment. It was found that main reaction mechanism occurred in the plasma electro-catalysis system was non-thermal pyrolysis rather than transesterification. The main reactions within the plasma treatment were due to collision between high energetic electrons (supplied from high voltage power supply through high voltage electrode) and the reaction mixtures. The high energetic electrons affected the electrons pair of covalent bonding to be excited or dissociated even ionized at higher energy. Therefore, this plasma electro-catalysis system was promising for biodiesel synthesis from vegetable oils due to only very short time reaction was needed, even no need a catalyst, no soap formation, and no glycerol by-product. This system could produce fatty acid methyl ester yield of 75.65% at 120 seconds and other possible chemicals, such as alkynes, alkanes, esters, carboxylic acid, and aldehydes. However, during the plasma process, the reaction mechanisms were still difficult to be controlled due the action of available high energetic electrons. The advanced studies on how to control the reaction mechanism selectively in the plasma electro-catalysis will be published elsewhere.

Keywords: plasma reactor; electro-catalysis; biodiesel; transesterification; cracking; energetic electrons

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1. Introduction

Recent worldwide energy policies and increased environmental concerns are driving industry to come up with an alternative fuels, such as biodiesel. Biodiesel is an alternative fuel consisting of fatty acid methyl esters (FAME) produced by transesterification of triglycerides, the main constituent of various kinds of vegetable oil. This renewable fuel can be used in any compression ignition engine without major modifications. Biodiesel fuel is defined as the alkyl esters of long chain fatty acids, which fulfills certain standards. The biodiesel chemical is obtained by the transesterification or alcoholysis of natural tri-acylglycerols or triglyceride with short-chain alcohols, usually methanol or ethanol. The

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triglyceride was obtained from various crude such as vegetable oils, animal fats, waste fats and greases, waste cooking oils or side-stream products of refined edible oil production.

The transesterification reaction requires the presence of a catalyst, which can be a base, an acid, or an enzyme to occur at an acceptable rate, although it can be conducted in non-catalytic but supercritical conditions [1,2]. The base and acid catalysts, most commonly used in biodiesel production, include both homogeneous and heterogeneous catalysts. Until now, homogeneous base catalysts (KOH or NaOH) have been well known used in industry, since the process has fast reaction rate at mild reaction conditions. Unfortunately, their utilization in vegetable oils transesterification has big problems including forming soaps as undesirable by-products in which large amounts of wastewater was resulted, corrosiveness, and needs longer time for separation process.

Therefore, the use of heterogeneous catalysts allows a more environmentally benign process to be used for biodiesel production. The use of heterogeneous catalysts could enhance efficiency of reactor design, enable continuous process, and improve the economics of biodiesel production. The use of heterogeneous catalysts does not produce soaps through free fatty acid neutralization, which simplifies the separation and purification processes. Due to the potential interest of heterogeneous catalyst usage, researches on the transesterification reaction using the solid catalysts for biodiesel production has increased over the past decade. Heterogeneous catalysts could overcome the mentioned problems of homogeneous catalysts usage. In fact, solid acid catalysts have been used in many industrial processes because they contain a variety of acid sites with different strength of Brönsted or Lewis acidity, compared to the homogenous acid catalysts.

Many kinds of solid catalysts for biodiesel production have been investigated by previous researchers including base and acid solid catalysts. The solid base catalyst includes CaO-based oxides [3,4], lithium-based [5], and zinc oxide-based catalysts [6-8]. Heterogeneous solid acid catalysts have been used as an alternative to basic and enzyme catalysts, since they can be used in both transesterification and esterification reactions [9]. However, the acid catalysts require high alcohol-to-oil molar ratios and catalyst concentrations to achieve satisfactory transesterification conversions. The solid acid catalysts include sulphated zirconia [9-12]. However, the use of solid acid and basic catalysts still have some problems, especially longer duration of reaction, mass transfer resistance between liquid oil and solid catalyst, and separation between phases.

Transesterification of vegetable oils to yield biodiesel can also be performed by microwave irradiation with acid, base, and heterogeneous catalysts [13,14], as well as ultrasonic-assisted catalysis [15,16]. Production of biodiesel by transesterification reaction under microwave irradiation is effective in accelerating the reaction rate. Microwave effect on the transesterification reaction includes enhancement of reaction by a microwave thermal effect. The microwave heating shows a promising technique for biodiesel production in a short reaction time with high product yield. In term of ultrasound technology in biodiesel processing, the use of sonochemistry is also applied in biodiesel production as the ultrasonic field is known to produce chemical and physical effects that arise from the collapse of cavitation bubbles. Low frequency sonication can be used to produce emulsions from immiscible liquids and since oil and alcohol are immiscible, this effect could be employed for biodiesel preparation. Production of biodiesel under ultrasonic processing possesses the following advantages: reduction in processing time, amount of alcohol and catalyst required, separation time and reaction temperature [15].

Another promising method is the use of plasma technology, whether plasma electro-catalysis or using integrated plasma assisted – catalyst [17-21] that had been applied for other synthesis. Over the past decade, non-thermal plasmas have been investigated as a way to catalyze the conversion processes of various hydrocarbon fuels into syngas. The non-thermal plasmas are electrically-driven ionized gases that are known to generate chemically active species, such as O and OH, which can act as chain-branching radicals that assist with the propagation of fuel conversion reactions and can lower the temperature required for a reaction to proceed. For this reason, some researchers believed that the non-thermal plasma has a catalytic effect assisting the fuel conversion processes. In plasma processes for the biodiesel production by methanolysis of vegetable oils, electro-chemical reaction is expected to split carbon-carbon bonds within the triglyceride reactants, unlike conventional processes that break weaker carbon-oxygen bonds. Carbon-to-carbon bonds are much stronger and require higher catalytic energy than available in conventional homogeneous and heterogeneous catalysis. The higher electro-chemical catalytic energy also enables addition reaction, attacking the unsaturated double bonds of triglycerides through oxygenation [17,22-24]. Oxygen molecules can be supplied by methanol during reaction process, which replace each carbon-carbon double bond to yield a saturated molecule that having better thermal storage stability. A high voltage power supply is required to store more high energetic electrons that help catalysing the methanolysis of triglyceride. However, the detailed mechanisms of the plasma catalysis effect are still unknown. Possible reaction mechanism during the plasma treatment is very important to be known in order to obtain the optimum operating conditions. Therefore, further study on high voltage plasma treatment of vegetable oil to produce biodiesel is importantly required.

The aim of this paper is to study biodiesel synthesis reaction routes from palm oil using plasma electro-catalysis process over Dielectric-Barrier Discharge (DBD) plasma reactor. The study was focused on finding possible reaction mechanism route during plasma electro-catalysis process. The prediction was performed based on the changes of GC-MS and FT-IR analyses to the biodiesel products with respect to time length of plasma treatment.

2. Materials and Methods

2.1. Materials

Commercial refine palm oil was purchased from local market (Tropicana ®) to be used as raw material of triglyceride, while methanol (Merck, 99.9%) were used as reactant.

2.2. Plasma Electro-Catalysis Process

Plasma electro-catalysis reaction of triglyceride with methanol was performed in a Dielectric Barrier Discharge plasma reactor. The DBD plasma reactor was composed of a high voltage electrode, a ground electrode, and a barrier of glass material. The glass barrier, like a dielectric, was placed adhere to ground electrode. The reactor was equipped with DC type high voltage power supply (support up to 15 kV), a high voltage probe (SEW PD-28), and multimeter (Sanwa) to measure the voltage during the reaction process. The high energetic electrons flowed from high voltage electrode to ground electrode through the glass barrier. The glass barrier was purposed to distribute the electrons flowed toward ground electrode.

The plasma electro-catalysis was conducted by filling the reactor with palm oil and methanol with methanol to oil mole ratio of 6:1. Thus, the reactor was heated up to 65 ^{o}C, which in turn a DC 10 kV high voltage was applied on the electrode. In this reactor, distance between both electrodes was 1.5 cm, while the ground electrode was connected to earth ground. Effect of discharge duration was studied by varying the reaction or contact time as 30, 120, and 300 seconds, while the methanol to oil mole ratio, voltage, and gap of electrodes were kept constant at 6:1, 10 kV, and 1.5 cm, respectively. Effect of high voltage was investigated by varying voltage as 6, 8, and 10 kV, while the methanol to oil mole ratio, reaction duration, and gap of electrodes were kept constant at 6:1, 120 seconds, and 1.5 cm, respectively. Effect of distance between electrode was investigated by varying the electrodes gap as 1.5, 2.5, and 3.5 cm, while the methanol to oil mole ratio, voltage, and reaction duration were kept constant at 6:1, 10 kV, and 120 seconds, respectively.

2.3. Biodiesel Product Characterization

In order to predict the possible reaction routes during plasma electro-catalysis process, the biodiesel product was analyzed by using GC-MS for identification of FAME components (ASTM E202), and FT-IR for identification of chemical structures (ASTM E168) analysis. Beside the components and chemical structure identification, other analysis of important biodiesel characteristics were also performed, they are: density (ASTM D1298), viscosity (ASTM D445), acid value (FBI-A01-03), cetane number (ASTM D613), and heating value (ASTM D1405).

3. Results and Discussion

3.1. Prediction of Reaction Routes within-Plasma Electro-Catalysis System

Possible reaction routes within plasma process is essentially different with other conventional catalytic reactions. Initially, the energetic electrons collide with the liquid bulk molecules resulting in excitation, dissociation, and/or ionization, and the formation of atoms and metastable compounds. When the electric field is high enough to lead breakdowns, a large number of micro-discharges are produced. Thus, these active atoms and metastable compounds subsequently collide with reactant molecules. According to this mechanism, various reactions may occur and mixture of compounds with various compositions may be consequently produced [20,21].

In this plasma electro-catalysis experiments, the reaction products were analyzed using GC-MS and was confirmed with FT-IR spectra. In fact, reaction between triglyceride and methanol with the presence of high energetic electrons from plasma system at mild duration (120 seconds) can produce various chemicals, i.e. fatty acid methyl ester, aldehydes, alkynes, alcohols, esters, and carboxylic acids as presented in Figure 1 and Table 1. From Figure 1 and Table 1, various fatty acid methyl esters were detected, i.e. pentadecanoic acid methyl ester ($C_{17}H_{34}O_2$); 9,12-octadecadienoic acid methyl ester ($C_{19}H_{34}O_2$); 9-octadecenoic acid methyl ester ($C_{19}H_{36}O_2$); pentadecanoic acid methyl ester ($C_{17}H_{34}O_2$); and 9-octadecenoic acid hexyl ester ($C_{24}H_{46}O_2$). Meanwhile, other chemicals were also resulted for 30 seconds reaction time by plasma electro-catalysis process, they were: 1-heptyne (alkyne), octadecanoic acid (carboxylic acid), 1-hexadecanol, and 9-octadecenal (aldehyde). At reaction time of 120 seconds, the following chemicals were also detected, i.e.: 1-heptyne (alkynes), isooctanol (alcohol), hexadecenoic acid (carboxylic acid), octadecanal and 9-octadecenal (aldehydes). Other chemicals, such as gases, were also produced as bubble within reactor and indicated by increasing reactor pressure.

The detected chemicals as revealed by the GC-MS were confirmed with FT-IR from chemical structure point of view as depicted in Figure 2 and Table 2. From Figure 2 and Table 2, the detected chemical bondings include: C-H, $-CH_3$, C=O, C-O, C-C, dan O-H. From the facts of IR spectra and confirmed with GC-MS, the following chemicals were predicted, i.e. fatty acid methyl esters, aldehydes, alkynes, alcohols, esters, and carboxylic acids. Fatty acid methyl esters were formed during reaction implied from the following IR spectra as listed in Table 2, i.e.: stretching mode of C-H alkane and C-H alkene, bending mode of C-H alkane, stretching mode of C=O, stretching mode of C-C and C=O. Alkyne compounds were indicated from stretching mode of C=O, stretching mode of C-H, stretching mode of C≡C, and bending mode of C-H. Alcohol compounds were suggested from detected C-H stretching, C-H bending, C-O stretching, C-C stretching, and O-H stretching. In term of carboxylic acid possibility, stretching and bending modes of C-H, stretching mode of C-O and C=O, and stretching mode of C-C and O-H indicate the presence of carboxylic acids.

According to the GC-MS and FT-IR identifications as aforementioned, the possible reaction routes occurred in the plasma electro-catalysis system is non-thermal cracking or pyrolysis due to collision between high energetic electrons from plasma source and the reaction mixture. The high energetic electrons

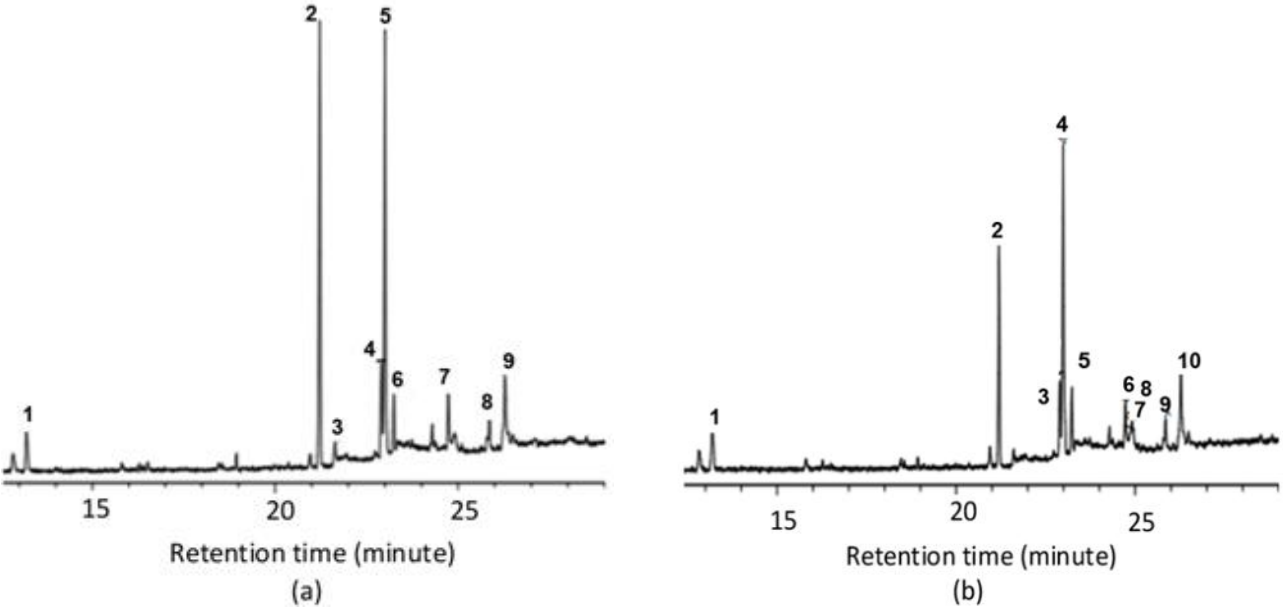


Figure 1. GC-MS Chromatogram of identified chemical components (mainly fatty acid methyl ester). (a) reaction time 30 seconds, (b) reaction time 120 seconds

Table 1. Identification and composition of GC-MS chromatogram at respected reaction time

Reaction Time (s)	Peak	Identified Chemical Components		Composition (wt%)
		Chemical Formula	Chemical Compound	
30	1	C_7H_{12}	1-Heptyne	4.91
	2	$C_{17}H_{34}O_2$	Pentadecanoic Acid Methyl ester	30.60
	3	$C_{18}H_{36}O_2$	Octadecanoic Acid	2.15
	4	$C_{19}H_{34}O_2$	9,12-Octadecadienoic Acid Methyl ester	7.13
	5	$C_{19}H_{36}O_2$	9-Octadecenoic Acid Methyl ester	33.12
	6	$C_{17}H_{34}O_2$	Pentadecanoic Acid Methyl ester	4.15
	7	$C_{16}H_{34}O$	1-Hexadecanol	4.66
	8	$C_{24}H_{46}O_2$	9-Octadecenoic Acid Hexyl ester	3.48
	9	$C_{18}H_{34}O$	9-Octadecenal	9.80
			Total	100.00
120	1	$C_{12}H_{12}$	1-Heptyne	7.17
	2	$C_{17}H_{34}O_2$	Pentadecanoic Acid Methyl ester	22.00
	3	$C_{19}H_{34}O_2$	9,12-Octadecadienoic Acid Methyl ester	8.06
	4	$C_{19}H_{36}O_2$	11-Octadecenoic Acid Methyl ester	36.43
	5	$C_{17}H_{34}O_2$	Pentadecanoic Acid Methyl ester	7.05
	6	$C_{16}H_{18}O$	Isooctanol	4.91
	7	$C_{10}H_{18}O_2$	7-Nonenoic Acid Methyl ester	2.11
	8	$C_{16}H_{30}O_2$	9-Hexadecenoic Acid	2.53
	9	$C_{16}H_{36}O$	Octadecanal	2.22
	10	$C_{18}H_{34}O$	9-Octadecenal	751
			Total	100.00

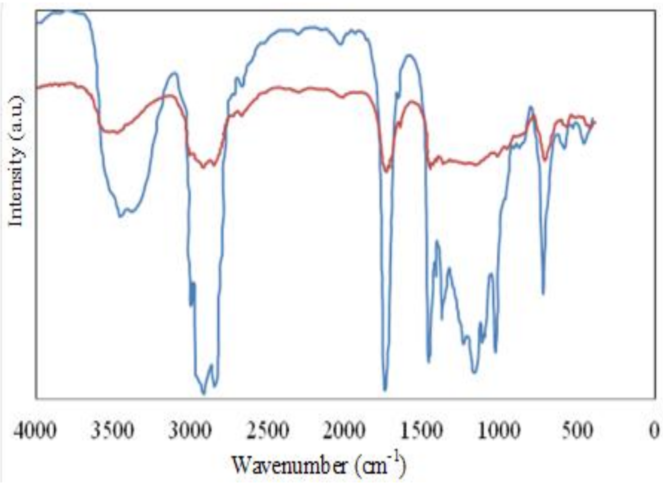


Figure 2. FT-IR spectra of plasma electro-catalysis products

Table 3. Chemical bondings energy (23,24)

No.	Bonding types	Chemical bonding energy (eV)
1	C-C	3.6
2	C-O	3.7
3	C-H	4.3
4	H-H	4.5
5	O-CO	4.8
6	C=C	6.3
7	C=O	7.7
8	C≡C	8.7

Table 2. Identification of vibrational mode of atomic bonding in reaction products

No	Detected peaks at wavenumber (cm^{-1})		Vibrational mode of IR detection	Type of possible chemical compounds
	30 seconds Reaction Time	120 seconds Reaction Time		
1.	2853, 2922	2853, 2922	C-H Alkane (Stretching)	Ester, FAME, alkane, alkyne, alcohol, aldehyde, carboxylic Acid
2.	1377, 1418	1415, 1438	C-H Alkane (Bending)	Ester, FAME, alkane, alkyne, alcohol, aldehyde, carboxylic acid
3.	3005	3005	C-H Alkane (Stretching)	Ester, FAME, alkane, alkyne, alcohol, aldehyde, carboxylic acid
4.	2166	2160	C≡C (Stretching)	Alkyne
5.	1748	1740	C=O (Stretching)	FAME, ester, carboxylic acid, aldehyde
6.	1032, 1098, 1117, 1165, 1238	1032, 1119, 1171, 1233	C-O (Stretching)	Alcohol, ester, FAME, carboxylic acid
7.	3381, 3466	3472	O-H (Stretching)	Alcohol, carboxylic acid
8.	1456	1455	C-C (Stretching)	Ester, FAME, alkane, alkyne, alcohol, aldehyde, carboxylic acid

supplied from high voltage power supply are able to affect the electrons pair of covalent bondings to be excited or dissociated even ionized depending on their energy. The vibration of electron pairs due to high energetic electrons effects is dependent on chemical bonding energy (listed in Table 3) [24,25] as compared to energy brought by the energetic electrons. Therefore, the plasma electro-catalysis could able to break the chemical bonding to produce the various chemicals. Types and composition of resulted compounds are dependent on the power of plasma or energetic electrons and reactor configuration/design.

Another possible reaction mechanism is transesterification reaction which is catalyzed by the energetic electrons. However, with respect to resulted compounds, non-thermal cracking mechanism is dominant rather than transesterification mechanism. The resulted compound groups, such as fatty acid methyl esters, aldehydes, alkynes, alcohols, carboxylic acids, and esters, were formed due to breaking and reforming of chemical bonding during the reaction time. Various chemicals were formed during the plasma electro-catalysis system at 30 and 120 seconds contact time which may be due to continuing chain chemical reactions. The drawbacks of this plasma electro-catalysis are how to control the reaction mechanism, how to drive which bonds will be excited or ionized, and when to stop the plasma electro-catalysis process. In order to avoid the chain reactions, the plasma electro-catalysis should be terminated at very short time of reaction, but the electrons should be having high energy to do the expected reaction mechanism. The higher energetic electrons could be produced by applying higher voltage by power supply and low current.

As mentioned before, the possible dominant reaction routes in this plasma electro-catalysis system was non-thermal cracking or pyrolysis. The possible reaction mechanism in this system was predominantly controlled by higher electrons energy from high voltage electrode than chemical bonding within reaction mixture. The energetic electrons from high voltage electrode have internal energy about 1-10 eV [24] leading to the chemical bonding energy. This electrons energy should be higher than chemical bonding energy to make sure that the covalent bonding to be cracked. Unfortunately, which covalent bonding would be cracked cannot be controlled easily, like in conventional catalysis system. Atomic covalent bonding with lower bonding energy is easier to be cracked than the higher bonding energy.

The following are predicted reactions route and mechanism during the plasma electro-catalysis system of palm oil and methanol:

1. Methanol was collide with high energetic electrons to form excited and dissociated groups or atoms (CH_3^*, OH^*, H^*, CH_3O^*) as depicted in Equation (1).

$$CH_3\text{-}OH + e \rightarrow CH_3^* + OH^* + H^* + CH_3O^* \qquad (1)$$

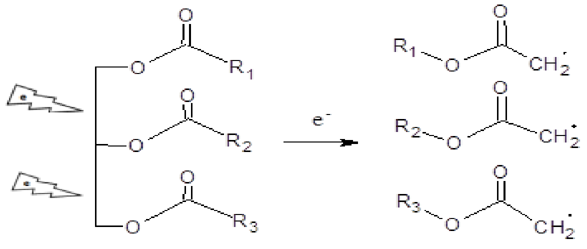
2. High energetic electrons cut the C-C bonding (3.3 eV) within triglyceride which in turn react with H^* from methanol to form methyl ester as described in Equations (2)

and (3).

3. Due to long duration of electrons collision, the fatty acid methyl ester may undergo continuing cracking of C-C and C-O bonding leading to shorter C-C bonding. In this case, formed FAME may undergo continuing cracking or pyrolysis due to too long duration of electrons collision leading to other detected chemicals such as aldehydes, alcohols, esters, and carboxylic acids. The continuing electrons cracking may be caused by higher energy content of electrons and the avalanche electrons. From this phenomena, control of contact time between high energetic electrons and the reactants is very important to favor which chemicals would be produced.
4. The predicted aldehydes formation was implied from scission of C-O bonding in alkyl ester groups and reacted with H^* from methanol to form aldehydes compounds as described in Equations (4) and (5). This reaction mechanism prediction is also confirmed by detected long-chain aldehydes. Therefore, formation of aldehyde compounds is due to scission of C-O in methyl ester.
5. Alkyne compounds (1-heptyne) may be formed from C-C scission in end section of methyl ester chain and reacts with CH^* from methanol as predicted in Equations (6) and (7).
6. Alcohols (1-hexadecanol) may be formed due to continuing reaction of Equation (6) with OH^* radical as predicted in Equation (8).
7. Some esters (9-octadecenoic acid hexyl ester) are detected due to continuing reaction between result of scission of C-O with product of Equation (6) as predicted in Equations (9) and (10).
8. Carboxylic acid (octadecanoic acid) may be formed in the plasma electro-catalysis system due to reaction between result of Equation (9) with H^* from methanol. This route was predicted in Equations (11) and (12). The acid was also formed due to reaction between result of Equation (4) with OH^* from methanol.

3.2. Potential of Plasma Electro-Catalysis System for Biodiesel Production

Various plasma sources are currently used for plasma-assisted reactions. Among those, DBD was exclusively used because of its several benefits. The DBD plasma reactor has a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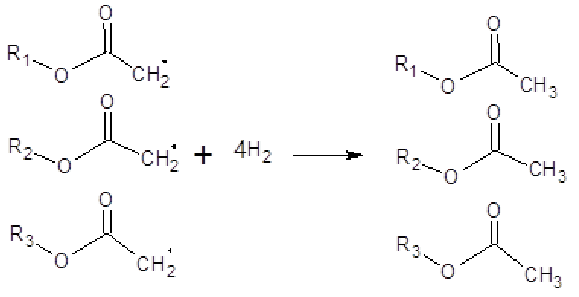
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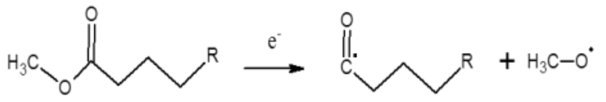
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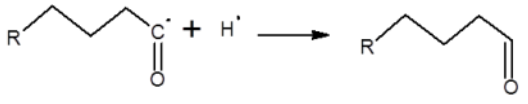
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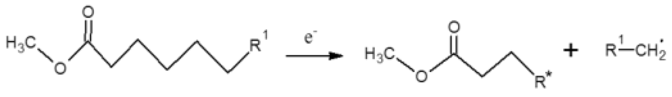
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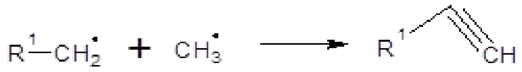
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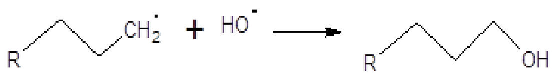
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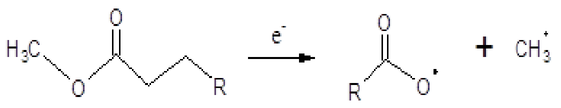
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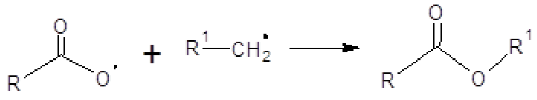
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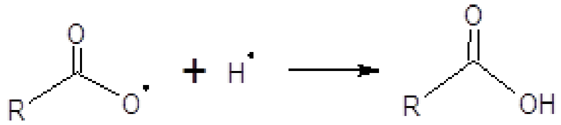
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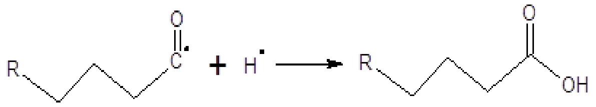
(12)

long and proven history originating from ozone synthesis [21]. Its fundamental of physical and chemical properties were well understood. This fact indicates that DBD is scalable technology to treat large amounts of gaseous materials. The DBD only slightly transits to unstable spark or arc plasma because of the presence of a dielectric barrier between the gaps. Great flexibility also exists in terms of electrode and reactor configurations. Therefore, the combination of DBD plasma reactor and catalysis is promising in term of plasma-assisted catalysis [17,18,20]. Moreover, the reactor can be constructed using inexpensive materials, such as glass and polymers. In terms of gas processing, partially excited, dissociated, and ionized gas, in which the gas temperature remains near room temperature, is readily created using simple electrode configuration and inexpensive power sources. High-energetic electrons produced by high voltage electric fields with low current collide against neutral molecules, producing ions, radicals, and electrically/vibrationally excited species almost independently of the reaction temperature [24]. These species are responsible for triggering fuel conversion at low temperatures.

The electro-catalysis phenomena within methanolysis reaction of triglyceride over DBD plasma reactor was investigated in this paper. The energetic electrons supplied by DC type - high voltage power supply collide with bulk liquid of mixed triglyceride - methanol to produce other valuable chemicals. In this non-thermal system, the bulk liquid only heated up to about 65 ^{o}C which is very far from electrons temperature of about 10^4 K. Consequently, this electro-chemical reaction is expected to split carbon-carbon bonds within the triglyceride reactants, unlike conventional processes that break weaker carbon-oxygen bonds. In fact, carbon-to-carbon bonds are much stronger and require higher energy to cut than that in conventional homogeneous and heterogeneous catalysis. The strong electro-chemical catalytic energy also enables and addition reaction, attacking the unsaturated double bonds of triglycerides through oxygenation. Oxygen molecules can be supplied by methanol during the reaction process, which replace each carbon -carbon double bond to yield a saturated molecule that having better thermal storage stability.

The plasma electro-catalysis system is promising for biodiesel synthesis from vegetable oils due to very short time reaction (main feature of plasma technology), even no catalyst required, no soap formation, and no glycerol by product. From the experimental works, it could produce fatty acid methyl ester yield of 75.65 % at 120 seconds and there was no glycerol and soap resulted. However, control of reaction mechanism due to the high energetic electrons within the plasma was very difficult to be done. The important think is how to avoid continuing reactions due the action of high energetic electrons. The recommendation for operating the plasma reactor is short duration contact between the energetic electrons and the reaction mixture, but the voltage should be very high at lower current. This suggestion is purposed to avoid continuing sustained chain reactions by applying very high energetic electrons at very short contact time.

3.3. Characterization of Biodiesel Product

Resulted biodiesel, mainly composed of fatty acid methyl esters as well as other chemical formed, was characterized in terms of density, kinematic viscosity, acid number, cetane

Table 4. Characterization of biodiesel product and its comparison with Indonesian National Standard (SNI-04-7182-2006)

Parameters	Experimentals	SNI Standard
Density (g/ml)	0.90	0.85 – 0.89
Kinematic Viscosity (cSt)	20	2.3 – 6.0
Acid Number (-)	0.671	max 0.8
Cetane Number (-)	51.73	min 51
Iod Value (-)	97.65	max 115
Saponification Number (-)	199.44	261.26
Calorific Value (cal/gr)	9105	-

number, iod value, saponification number, and calorific value as listed in Table 4. All parameters fulfil the requirement of biodiesel as Indonesian National Standard (*Standar Nasional Indonesia* - SNI-04-7182-2006) except for kinematic viscosity and density. The high viscosity of biodiesel product is due to formation of 1-hexadecanol, 9-octadecenal, and octadecanal that having high melting point. The unexcpected compounds are soluble in the biodiesel product that cause high viscosity and density. It is suggested that continuing reaction during plasma electro-catalysis should be avoided. The recommendation for applying the plasma electro-catalysis reactor is shorter duration of contact between the energetic electrons and the reactions mixtures at very high voltage and lower current.

4. Conclusion

The plasma electro-catalysis system was promising for biodiesel synthesis from vegetable oils due to only very short time reaction, even no catalyst required, no soap formation, and no glycerol by product. From the plasma electro-catalysis experiments, it can produce fatty acid methyl ester yield of 75.65 % at short reaction time of 120 seconds and there was no gliserol and no soap resulted. However, other chemicals may be resulted such as alkanes, alkynes, aldehydes, esters, and carboxylic acids. Control of reaction mechanism in plasma electro-catalysis was very important due to the high energetic electrons within plasma. The important idea was how to avoid continuing reactions due the action of high energetic electrons. Short duration contact between the energetic electrons and the liquid reactants was recommended, but the plasma electro-catalysis reactor should be operated at very high voltage and lower current. The purpose of the suggestion was to avoid continuing chain reactions by applying very high energetic electrons at very short contact time.

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References

[1] Macario, A., Giordano, G., Onida, B., Cocina, D., Tagarelli, A., Giuffrè, A.M. (2010). Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst. *Appl. Catal. A Gen.* 378(2): 160-168.

[2] Yusuf, N.N., Kamarudin, S.K., Yaakub, Z. (2011). Overview on the current trends in biodiesel production. *Energy Convers. Manag.* 52(7): 2741-2751.

[3] Kouzu, M., Hidaka, J. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. *Fuel.* 93: 1-12.

[4] Taufiq-Yap, Y.H., Lee, H.V., Hussein, M.Z., Yunus, R. (2011). Calcium-based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. *Biomass Bioenergy* 35(2): 827-834.

[5] Istadi, I., Pramudono, B., Suherman, S., Priyanto, S. (2010). Potential of $LiNO_3/Al_2O_3$ Catalyst for Heterogeneous Transesterification of Palm Oil to Biodiesel. *Bull. Chem. React. Eng. Catal.*, 5(1): 51-56

[6] Islam, A., Taufiq-Yap, Y.H., Chu, C.M., Chan, E.S., Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Saf. Environ. Prot.* 91(1-2): 131-144.

[7] Kesić, Ž., Lukić, I., Brkić, D., Rogan, J., Zdujić, M., Liu, H., et al. (2012). Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis. *Appl. Catal. A Gen.* 427-428: 58-65.

[8] Lukić, I., Kesić, Ž., Maksimović, S., Zdujić, M., Liu, H., Krstić, J., et al. (2013). Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO·ZnO. *Fuel.* 113: 367-378.

[9] Nandagopal, J., Subramanian, S. (2010). Synthesis of Biodiesel from Neem Oil using Sulfated Zirconia via Transesterification. *Brazilian J. Chem. Eng.* 27(04): 601-608.

[10] Lam, M.K., Lee, K.T. (2010). Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid acid sulfated tin oxide catalyst. *Fuel.* 89(12): 3866-3870.

[11] Rattanaphra, D., Harvey, A.P., Thanapimmetha, A., Srinophakun, P. (2012). Simultaneous transesterification and esterification for biodiesel production with and without a sulphated zirconia catalyst. *Fuel.* 97: 467-475.

[12] Reddy, B.M., Sreekanth, P.M., Lakshmanan, P. (2005). Sulfated zirconia as an efficient catalyst for organic synthesis and transformation reactions. *J. Mol. Catal. A: Chem.* 237: 93-100.

[13] Azcan, N., Yilmaz, O. (2012). Microwave Irradiation Application in Biodiesel Production from Promising Biodiesel Feedstock: Microalgae (Chlorella protothecoides). *Proc. World Congr. Eng. Comput. Sci.* San Fransisco, USA.

[14] Gude, V., Patil, P., Martinez-Guerra, E., Deng, S., Nirmalakhandan, N. (2013). Microwave energy potential for biodiesel production. *Sustain. Chem. Process.* 1(5): 1-31.

[15] Babajide, O., Petrik, L., Amigun, B., Ameer, F. (2010). Low-Cost Feedstock Conversion to Biodiesel via Ultrasound Technology. *Energies.* 3(10): 1691-1703.

[16] Veljković, V.B., Avramović, J.M., Stamenković, O.S. (2012). Biodiesel production by ultrasound-assisted transesterification: State of the art and the perspectives. *Renew. Sustain. Energy Rev.* 16(2): 1193-1209.

[17] Lee, D.H., Kim, T. (2013). Plasma-catalyst hybrid methanol-steam reforming for hydrogen production. *Int. J. Hydrogen Energy.* 38(14): 6039-6043.

[18] Gallagher, M.J., Geiger, R., Polevich, A., Rabinovich, A., Gutsol, A., Fridman, A. (2010). On-board plasma-assisted conversion of heavy hydrocarbons into synthesis gas. *Fuel.* 89(6): 1187-1192.

[19] Rafiq, M.H., Hustad, J.E. (2011). Biosyngas production by autothermal reforming of waste cooking oil with propane using a plasma-assisted gliding arc reactor. *Int. J. Hydrogen Energy.* 36(14): 8221-8233.

[20] Nozaki, T., Okazaki, K. (2013). Non-thermal plasma catalysis of methane: Principles, energy efficiency, and applications. *Catal. Today.* 211: 29-38.

[21] Istadi, I., Saidina Amin, N.A. (2006). Co-generation of synthesis gas and C2+ hydrocarbons from methane and carbon dioxide in a hybrid catalytic-plasma reactor: A review. *Fuel.* 85(5-6): 577-592.

[22] Motasemi, F., Afzal, M.T. (2013). A review on the microwave-assisted pyrolysis technique. *Renew. Sustain. Energy Rev.* 28: 317-330.

[23] Rahimpour, M.R., Jahanmiri, A., Mohamadzadeh Shirazi, M., Hooshmand, N., Taghvaei, H. (2013). Combination of non-thermal plasma and heterogeneous catalysis for methane and hexadecane co-cracking: Effect of voltage and catalyst configuration. *Chem. Eng. J.* 219: 245-253.

[24] Fridman, A. (2008). *Plasma Chemistry*. Cambridge: Cambridge University Press; p. 978.

[25] Sanderson, R.T. (1983). *Polar Covalence*. London: Academic Press; p. 240.