

SYNTHESIS OF BIODIESEL ON A HYBRID CATALYTIC-PLASMA REACTOR OVER $K_2O/CaO-ZnO$ CATALYST

Luqman Buchori, Istadi Istadi^{*}, Purwanto Purwanto

Diponegoro University, Faculty of Engineering, Department of Chemical Engineering, Jl. Prof. Soedarto, SH, Semarang 50275, Indonesia

*Corresponding author: istadi@live.undip.ac.id

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Abstract: This paper aimed to study the synergistic effects of dielectric barrier discharge plasma and 5 % $K_2O/CaO-ZnO$ catalyst on biodiesel synthesis. The catalyst was prepared using co-precipitation followed by impregnation method. The catalyst was characterized by XRD, while the catalyst basicity was tested by titration method. The effects of voltage, weight hourly space velocity (WHSV), and catalyst pellet diameter on the yield of fatty acid methyl ester (FAME) and biodiesel were studied. The transesterification process within and without plasma environment was investigated to find synergistic effect between the role of high energetic electrons from the plasma through the catalytic reaction zone and the role of basicity in the catalyst. From the results, an applied voltage of 5 kV, a WHSV of 1.186 min^{-1} , and a catalyst diameter of 5 mm gave the better FAME yield of 77.19 %. The reaction time required was only 1.25 minutes at a discharge power of 530 W. This result proved that the plasma environment has a significant effect on performance of the hybrid catalytic-plasma reactor for biodiesel production.

Keywords: *basicity, biodiesel, catalytic-plasma reactor, fatty acid methyl ester, $K_2O/CaO-ZnO$ catalyst, synergistic effect*

INTRODUCTION

Biodiesel is an alternative fuel instead of diesel oil due to quite similar in main characteristics. The biodiesel is better than diesel oil in some aspects, such as renewable resource, biodegradable, non-toxic, safe, lower emission, no sulfur, no aromatic, higher cetane number, high flash point (>130 °C) and eco-friendly [1]. The biodiesel can be produced by dilution, thermal cracking (pyrolysis), microemulsion, and transesterification. The best method for producing higher quality biodiesel is transesterification [2]. The transesterification process, a reaction between fat or oil and alcohol to form esters, is affected by various factors including moisture content, free fatty acid, type of catalyst, concentration of catalyst, molar ratio of alcohol/oil, kind of alcohol, reaction time, reaction temperature, mixing intensity, and using organic cosolvents [3]. The homogeneous transesterification process provides a good yield of biodiesel although some limitations were found, i.e., complexity of purification and separation stages of the product, disposal of basic and acid wastewater, difficulty in glycerol recovery, high energy demand, and soap formation as a by-product [4, 5]. Meanwhile, the heterogeneous transesterification can overcome the problems within the homogeneous catalyst system in which there are different phases between catalysts and products so that the purification processes would be simpler. Therefore, the catalysts can be easily regenerated, recycled, and reused several times tailoring minimum material and process cost [1, 2, 6].

Only a few researchers have developed the advanced technology processes for biodiesel production, i.e., microwave, ultrasound, or plasma assisted processes, particularly for plasma-assisted technology. This novel technology only requires shorter reaction time, no soap formation, and even no by-product, i.e., glycerol [1, 7 - 11]. Istadi et al. [7] and Abdul-Majeed et al. [8] investigated the synthesis of biodiesel without the catalyst in a dielectric-barrier discharge (DBD). Lawson and Baosman [10] and Cubas et al. [11] studied the production of biodiesel using corona plasma reactors. This system was called an electro-catalysis plasma process. They found that the transesterification process using the electro-catalysis plasma process resulted in higher biodiesel yield, shorter reaction time, and easier biodiesel separation in comparison to the conventional path. However, the electro-catalysis plasma system (without catalyst) has several drawbacks, such as difficult to control the reaction mechanism, difficult to manage the excitation and occurring ionization from the bond electrons, and difficult to inhibit continuing reactions [1, 7].

The utilization of the catalyst within a plasma reactor was conducted by Hyun et al. [12] and Buchori et al. [9] for batch and continuous processes, respectively. Hyun et al. [12] utilizing KOH as a catalyst, while Buchori et al. [9] using the catalysts of active carbon and the modified active carbon. They reported that there is a synergistic effect of plasma and catalyst in the transesterification process to produce biodiesel. However, only a few researchers focused on the simultaneous catalysis and plasma processing, but they only focused on corona discharge plasma with a liquid catalyst and DBD plasma with acid-modified catalyst, respectively [9, 12]. There have been limited studies on simultaneous fixed-bed DBD plasma reactor using a basic catalyst. Therefore, the purpose of this research is to study the synergistic effect of basic catalysis and plasma processing on the improvement of biodiesel production yield over transesterification of vegetable oils with methanol. In this study, the effect of the applied voltage or the discharge power, the

weight hourly space velocity (WHSV), and the catalyst diameter on performance of the hybrid catalytic-plasma reactor for biodiesel synthesis over metal oxide catalyst ($K_2O/CaO-ZnO$) was investigated. This study also explores effect of catalyst basicity role on increasing the selectivity to biodiesel, especially fatty acid methyl esters (FAME).

MATERIALS AND METHODS

Materials of research

The raw materials used in this research were methanol (99.9 %) and soybean oil (MazolaTM Soya Bean Oil). The soybean oil was purchased from local market, while the methanol was purchased from Merck. The chemicals were purchased from Merck including calcium nitrate tetrahydrate (99 %), zinc nitrate tetrahydrate (98.5 %), sodium carbonate anhydrous (99 %), potassium nitrate (99 %), and sodium hydroxide (99 %).

Preparation of catalyst

The catalyst, $K_2O/CaO-ZnO$, was prepared by co-precipitation of CaO and ZnO using precursors solution to produce $CaO-ZnO$ and followed by impregnation of K_2O on the $CaO-ZnO$ catalyst. On the co-precipitation method, the 2 M solution of $Ca(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 4H_2O$ were dissolved in a distilled water. Both solutions were mixed so that the catalyst of $CaO-ZnO$ mixed metal oxide was prepared using Ca to Zn molar ratio of 3:1. The required amount of Na_2CO_3 for the co-precipitation process was dissolved in distilled water to make a 2 M Na_2CO_3 solution. Within the gel formation process, the solution was slowly dropped by $10 \text{ mL} \cdot \text{min}^{-1}$ into the mixed metal oxide solution with vigorously stirred. The pH of the ultimate solutions mixture was adjusted to 10 by adding 1 M $NaOH$. The resulted mixture was then stirred (200 rpm) for 24 h, while heating up at a temperature of $60 \text{ }^\circ\text{C}$. The solid product was then filtered and washed (several times) with distilled water until alkali-free (pH about 7). The precipitate was then dried in a Memmert oven overnight at a temperature of $110 \text{ }^\circ\text{C}$. The dried solid was then calcined in a Ney Vulcan box furnace at a temperature of $800 \text{ }^\circ\text{C}$ for 3 h. The obtained solid product, $CaO-ZnO$, was then impregnated by immersing into 0.5 M KNO_3 solution for 30 min while stirred and was then dried in the Memmert oven at a temperature of $110 \text{ }^\circ\text{C}$ overnight. The dried solid catalyst was then calcined at a temperature of $300 \text{ }^\circ\text{C}$ in the box furnace for 5 h (without air flowing). The resulted solid catalyst was called as 5 % $K_2O/CaO-ZnO$ or symbolized as 5KCZ. After that, the catalyst was crushed and then was pelleted into cylindrical pellets with a diameter (d_p) of 3, 5, and 7 mm. The adding K_2O component into the $CaO-ZnO$ catalyst was targeted to have bifunctional roles, i.e., acts as a binding agent and to increase basicity of catalyst.

Characterizations of catalyst and biodiesel product

Characterization of the 5KCZ catalyst was done with X-Ray Diffraction (XRD) for the respected crystal structure. In the XRD (Shimadzu XRD-7000) analysis, a $Cu-K\alpha$

radiation ($k = 1.54 \text{ \AA}$) was operated at 30 mA and 30 kV. The diffraction patterns were generated at 2θ angle ranges of 10° to 90° with a scanning speed of $4^\circ \cdot \text{min}^{-1}$ at ambient temperature. The diffractogram/peak was compared to the data from JCPDS (Joint Committee on Powder Diffraction Standards) library to specify the compounds of crystal in the catalyst.

Analysis of the products of biodiesel was made by using Gas Chromatography-Mass Spectrometry (GC-MS). A Gas Chromatography-Mass Spectrometry (QP2010S SHIMADZU, DB-1 column) analysis was used to determine the composition of biodiesel product. The samples were analyzed with 50°C oven temperature (hold for 5 min) and increased gradually by $10^\circ \text{C} \cdot \text{min}^{-1}$ to 260°C and held for 33 min. The yield (%) of FAME and biodiesel were determined using eqns. (1) and (2).

$$\text{Yield of FAME} = \frac{\% \text{FAME GC Area} \times \rho_{\text{biodiesel}} \times V_{\text{biodiesel}}}{\text{weight of soybean oil feed}} \times 100\% \quad (1)$$

$$\text{Yield of biodiesel} = \frac{\rho_{\text{biodiesel}} \times V_{\text{biodiesel}}}{\text{weight of soybean oil feed}} \times 100\% \quad (2)$$

Catalyst basicity test

Basicity of catalyst was determined by titration method, where the solid catalyst suspended in benzene was titrated with benzoic acid as introduced by Tanabe and Yamaguchi [13]. The powder catalyst was crushed and sieved to 100-200 mesh. One-half gram of the catalyst sample was put into an Erlenmeyer flask. Twenty mL of benzene and 1 mL of indicator solution (128 mg of bromthymol blue (BTB) in 100 mL of benzene) was poured into the Erlenmeyer flask. The catalyst sample suspension was changed from yellow dye to green-blue color. After that, the 0.1 N benzoic acid was added dropwise from the micro burette into the suspension. The green color of the solid particle gradually disappeared. The endpoint of titration was determined when all the green color disappeared. The basicity was calculated from the titer of 0.1 N benzoic acid required as shown in eqn. (3), where V denotes the volume of benzoic acid solution (mL), N denotes normality of benzoic acid solution ($\text{meq} \cdot \text{mL}^{-1}$), and W represents a weight of catalyst sample (g) [13].

$$\text{Basicity} (\text{mmol} \cdot \text{g}^{-1}) = \frac{(V \times N)_{\text{benzoic acid}}}{W_{\text{catalyst}}} \times 100\% \quad (3)$$

Configuration of the catalytic-plasma reactor system

A catalytic-DBD plasma reactor system was used in this research. The catalytic-plasma reactor consisted of a high voltage electrode, a barrier, a ground electrode, and a packed of catalyst within discharge zone. The high voltage electrode was made of the copper rod with a 0.5 cm in diameter and 30 cm in length. The ground electrode was made of stainless steel plate with a 3 cm in diameter. The glass barrier placed between both electrodes was acted as a dielectric-like element which made of a glass tube with a thickness of 0.1 cm and a diameter of 2.8 cm. The high voltage electrode was installed in the center of the ground electrode. The gap between electrodes, a distance between the high voltage electrode and the ground electrode, was 1.27 cm.

The high voltage applied on the catalytic-plasma reactor was supplied by a high voltage power supply (up to 18 kV and 330 W DC-type), and equipped with a high voltage probe (1000X, maximum 40 kV), and an electric split tube furnace. The temperature of the reactor was controlled and measured by a temperature controller (± 5 °C) connected to the electric tube furnace. A packed of cylindrical pellet catalyst was placed within a discharge zone (a zone between the high voltage electrode and the dielectric barrier) in the plasma reactor.

Discharge power measurement on the catalytic-plasma reactor

In this research, the electric source used in the hybrid catalytic-plasma reactor was direct current (DC) type. The discharge voltage, the current, and the electric power during the reaction process were measured by a digital oscilloscope (Tektronix TBS 1052B-EDU 50 MHz 1 GS/s). The discharge power (P , in W) was calculated by multiplying the voltage by the current as represented in eqn. (4).

$$P = VI \quad (4)$$

Measurement of discharge current (I), discharge voltage (V), and discharge power (P) was presented in Table 1.

Table 1. The magnitude of discharge power on the various voltage

Voltage [kV]	Current [mA]	Power [W]
4	74	296
5	106	530
6	124	744
7	157	1099
8	171	1368
9	193	1737

Biodiesel synthesis over catalytic-plasma reactor

The experimental rig scheme was illustrated in Figure 1. Reactants (methanol and soybean oil) with the molar ratio of methanol/oil of 15:1 were flowed into the mixing tank and vigorously stirred. Thus, the reactant mixture was fed into the catalytic-plasma reactor packed with the 15.15 gram of 5KCZ catalyst. The 5KCZ catalyst was located within discharge zone of the plasma reactor. The catalytic-plasma reactor was heated up to 65 °C and kept constant by using temperature control. A DC-type high voltage power supply was installed to provide a high voltage on the plasma reactor. The high energetic electrons, provided by the high voltage power supply, flowed from the high voltage electrode to the ground electrode through the glass dielectric barrier discharge. The dielectric could control and distribute the electrons throughout the discharge zone. The biodiesel product was collected in a tank of product and then was analyzed for the FAME composition. Effect of the applied voltage was studied by varying the voltage into 4, 5, 6, 7, 8, and 9 kV, while the methanol/oil molar ratio, the WHSV, and the catalyst diameter were kept constant at 15:1, 1.186 min⁻¹, and 5 mm, respectively. Meanwhile, the effect of WHSV was studied by varying it into 1.186, 1.295, 1.409, 1.685, and 2.042 min⁻¹, while the methanol/oil molar ratio, voltage, and catalyst diameter were kept constant at 15:1, 5 kV, and 5 mm. Another work, effect of the

catalyst diameter was investigated by varying the diameter (d_p) into 3, 5, and 7 mm, while the methanol/oil molar ratio, the applied voltage, and the WHSV were kept constant at 15:1, 5 kV, and 1.186 min^{-1} , respectively. Effect of the catalyst basicity was explored by comparing the transesterification process before and after impregnation by K_2O . Effect of the plasma role was studied by comparing the yield of transesterification process over the 5KCZ catalyst with and without plasma.

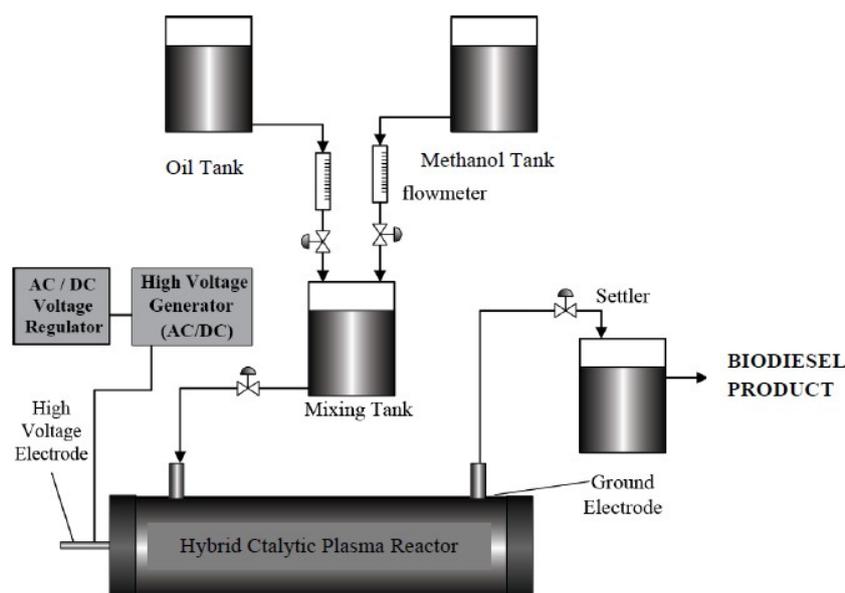


Figure 1. Scheme of transesterification process using hybrid catalytic plasma reactor

RESULTS AND DISCUSSION

Characterization of catalyst

X-ray Diffraction characterization

X-Ray Diffraction (XRD) pattern of the fresh and spent 5KCZ catalysts were illustrated in Figure 2. The XRD diffractogram of CaO was indicated by the intensity of the peaks at a 2θ angle of 17.8° , 28.6° , 33.6° , 50.7° , 63.2° , 64.2° and 67.9° (JCPDS File No. 37-1497) [14, 15]. The diffraction patterns of calcium oxide revealed cubic phase [16]. Meanwhile, the XRD pattern of ZnO exhibit crystalline phases at 31.7° , 34.4° , 36.2° , 47.5° , 56.5° , 62.8° , 69.02° , and 71.7° (JCPDS File No. 36-1451) [14–16]. The peaks at 2θ of 23.04° , 29.4° , and 39.4° correspond to K_2O (JCPDS File No. 47-1701; 77-2176) [14, 17]. This intensity peak presence is due to impregnation of K_2O on the surface of CaO-ZnO catalyst with K_2O loading of 5 wt. %. The high-intensity peak of K_2O showed that the K_2O was dispersed evenly on the surface of the catalyst. Based on the XRD pattern in Figure 2, the intensity of CaO and ZnO showed an increase, while the intensity of K_2O declined may be due to leaching process by methanol [16]. However, the diffraction peaks of CaO, ZnO, and K_2O on both catalysts were indicated by a similar pattern.

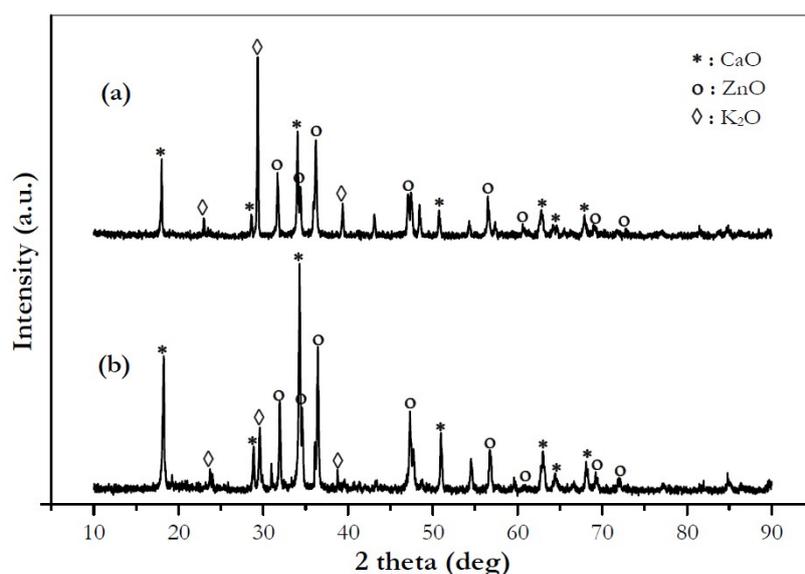


Figure 2. XRD pattern of the 5KCZ catalysts: (a) fresh, (b) spent

Catalyst basicity characterization

Characterization of the 5KCZ catalyst at various mole ratios of CaO-ZnO was illustrated in Figure 3. The figure shows XRD diffractogram of CaO, ZnO, and K₂O. The results of XRD diffractogram in accordance with the composition of the catalyst prepared. The highest intensity peak of CaO obtained at the mole ratio of CaO-ZnO catalyst of 3:1 that include 17.8°, 28.6°, 50.7° and 52.7° (JCPDS File No. 37-1497) [16]. On the CaO-ZnO mole ratio of 3:1, the intensity peak of K₂O spread on the surface of the catalyst at 2θ of 23.04°, 39.49°, 46.67°, and 48.88° (JCPDS File No. 47-1701; 77-2176) [14, 17].

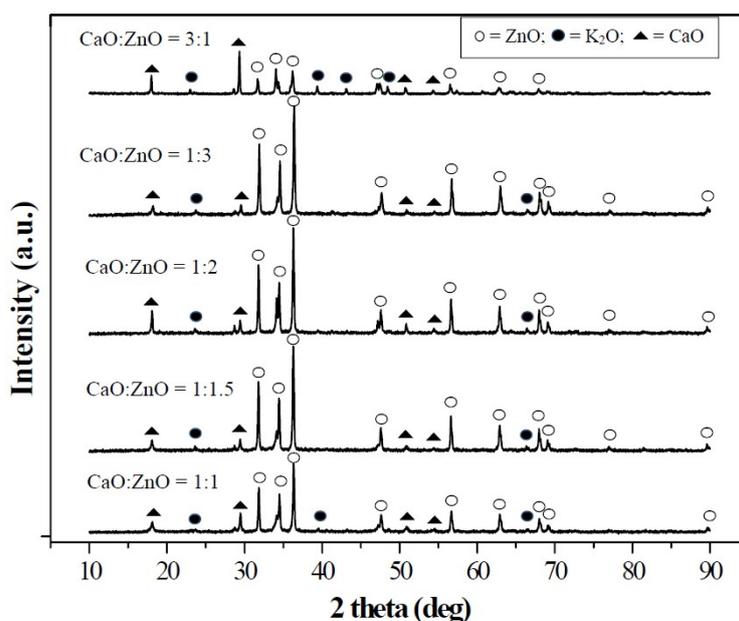


Figure 3. XRD pattern of the 5KCZ catalyst at various mole ratios of CaO-ZnO

Basicity of the CaO-ZnO catalyst at various mole ratios after impregnated with 5 % K₂O was presented in Table 2. The table indicates an increased basicity with respect to all the mole ratio of CaO-ZnO. The highest basicity obtained in CaO-ZnO mole ratio of 3:1. This is due to that the calcium oxide (CaO) has higher basic strength than ZnO. The greater the mole ratio of CaO in CaO-ZnO mixed metal oxide, the catalyst basicity would increase. The addition of K₂O on the CaO-ZnO catalyst enhances basicity of the catalyst.

Table 2. Basicity of CaO-ZnO catalyst (before and after impregnation with 5 % K₂O)

CaO:ZnO mole ratio	Basicity [mmol·g ⁻¹]	
	Before impregnation	After impregnation
1:1	0.344	0.504
1:1.5	0.260	0.316
1:2	0.164	0.280
1:3	0.088	0.230
3:1	0.662	1.090

Effect of applied voltage on performance of the catalytic-plasma reactor

The effect of applied voltage on FAME and biodiesel yields was shown in Figure 4. These yields were calculated using eqns. (1) and (2). From Figure 4, an increasing applied voltage of 4 to 5 kV increases the yield of FAME, however, continuing the increased applied voltage led to decreasing the yield of FAME. This fact indicates that the applied voltage gives significant effect on the performance of the catalytic-plasma reactor. Justification of the applied voltage effect on the improvement of biodiesel production yield is explained as follows. The high applied voltage supplied by a high voltage power supply would generate high energetic electrons. The electrons flowed from the high voltage electrode, collide with reactants on the surface of the catalyst, and reached the ground electrode. Within the discharge zone, the electrons pairs in covalent bonding of the reactant molecules could be interfered by the high energetic electrons. Therefore, due to incoming the photon energy from high energetic electrons, the electron pairs would be excited, dissociated, ionized, or even break carbon-carbon bond in triglycerides, thus forming a monoalkyl ester [7, 10].

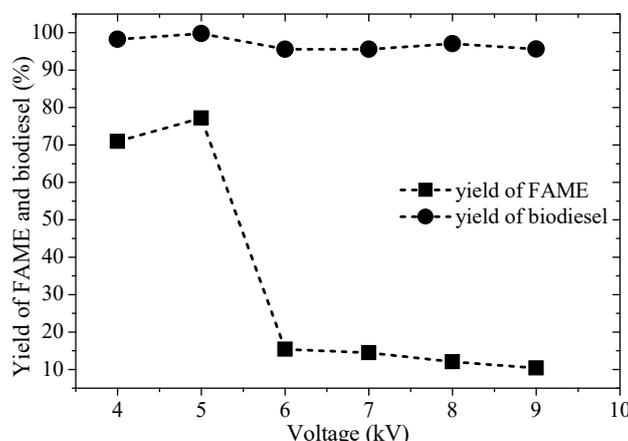


Figure 4. Effect of voltage on the FAME yield in hybrid catalytic-plasma reactor using 5KCZ catalyst ($d_p=5$ mm; CaO:ZnO=3:1; WHSV=1.186 min⁻¹)

The best FAME yield is 77.19 % obtained at 5 kV of an applied voltage. It is indicated that at a voltage of 4 kV, the hybrid catalytic-plasma process can produce FAME due to roles of the high energetic electrons on attacking the bonded electron pairs in triglyceride. However, this FAME yield was still low in comparison to the conventional process. A higher voltage was required to affect the bonded electron pairs in the triglycerides or reduced activation energy on the surface of the catalyst, leading to the maximum yield of FAME. Determination of biodiesel composition using GC-MS analysis on the applied voltage of 5 kV was presented in Table 3.

Table 3. Identification and composition of FAME product using GC-MS chromatogram

Chemical formula	Chemical compound	Composition [% area]
C ₁₉ H ₃₈ O ₂	octadecanoic acid, methyl ester	12.75
C ₂₁ H ₃₈ O ₂	11,14-eicosadienoic acid, methyl ester	10.31
C ₁₇ H ₃₂ O ₂	7-hexadecenoic acid, methyl ester	54.31
C ₁₈ H ₃₂	1,e-11,z-13-octadecatriene	22.62

The obtained fatty acid methyl ester components consist of octadecanoic acid methyl ester (C₁₉H₃₈O₂), eicosadienoic acid methyl ester (C₂₁H₃₈O₂), and hexadecenoic acid methyl ester (C₁₇H₃₂O₂). Moreover, another chemical formed during the plasma process is octadecatriene (C₁₈H₃₂) which may be due to the role of energetic electrons from plasma. At applied voltage higher than 5 kV, the catalytic-plasma process produces other unwanted chemicals that did not categorize as alkyl esters, such as oleic acid, aldehyde, linoleic acid, alkane, or alcohol. This fact may be due to vibration, excitation, dissociation, ionization, or even breaking the bonded electron pairs in reactants by the high energetic electrons from plasma at low energy consumption. The higher the applied voltage, various continuing chain reactions may occur leading to a processed mixture of compounds with different compositions. Therefore, it is difficult to control the reaction mechanism at higher applied voltage due to the action of high energetic electrons.

The applied voltage implemented to the high voltage electrode affects discharge power of a plasma reactor. Based on Table 1, the discharge power enhanced when the input applied voltage increased. High discharge power leads to generated more highly energetic electrons and ultimately produces a high degree of ionization in the plasma discharge. This phenomenon increases the collision frequency between active plasma species leading to higher conversion efficiencies [18]. However, in this study, discharge power required to get maximum yield of FAME was 530 W. Unfortunately, at discharge power higher than 530 W continuing reactions occur on producing other unexpected chemicals due to the action of abundant high energetic electrons.

Effect of weight hourly space velocity (WHSV) on performance of the catalytic-plasma reactor

The effect of WHSV and the time on stream on yields of FAME and biodiesel were presented in Figures 5 and 6, respectively. The WHSV is closely related to the residence time or time on stream relative to the weight of packed catalyst due to constitute the operating parameters of the most important in the biodiesel synthesis to determine the residence time. At higher WHSV, the time on stream becomes shorter. Figure 5 indicates that yield of FAME decreases with increasing the WHSV. That is, the FAME

yield increased with increasing time on stream. The principle of plasma system is a collision between high energetic electrons with electron pairs from covalent bonding in the reactant molecules to form monoalkyl esters. The higher WHSV, the shorter contact time between energetic electron and reactant molecules leading to the shorter the collision process. As a result, only a few bonded electron pairs in reactant molecules are excited to a decreased yield of FAME. It is indicated that the WHSV is significant parameters on operating the catalytic-plasma reactor system.

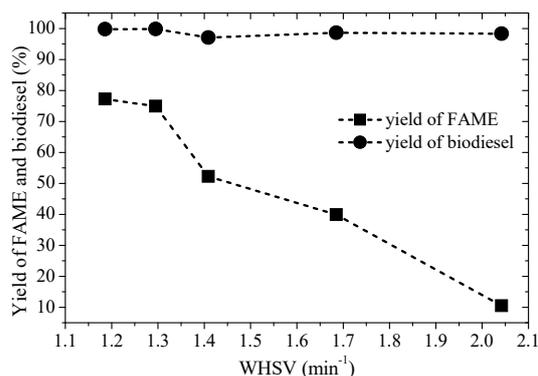


Figure 5. Effect of weight hourly space velocity (WHSV) on the FAME yield in a hybrid catalytic-plasma reactor using 5KCZ catalyst ($d_p=5$ mm; $CaO:ZnO=3:1$; $V=5$ kV)

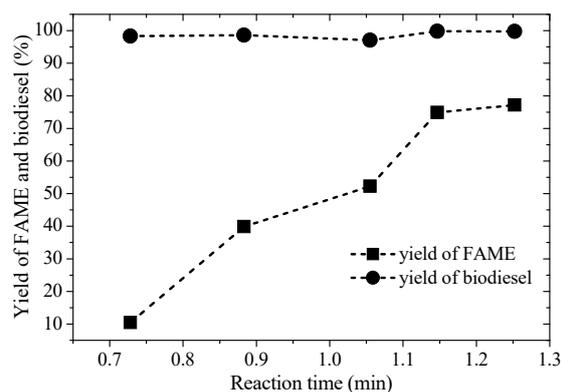


Figure 6. Effect of reaction time on the FAME yield in a hybrid catalytic-plasma reactor using 5KCZ catalyst ($d_p=5$ mm; $CaO:ZnO=3:1$; $V=5$ kV)

In the catalytic-plasma reactor system, the catalyst located in the discharge zone increases the contact time between high energetic electrons and reactant molecules [9] due to enhanced surface area of contact between the electrons and the reactants. As a result, the presence of catalyst within discharge zone would form active species in the discharge zone and the catalyst pores due to direct contact between the plasma and the catalyst [19]. The active species readily react with the adsorbed reactants on the surface of the catalyst which in turn create FAME and biodiesel products. At higher WHSV, the time on stream would be shorter within plasma reactor which in turn decreasing production of active species and reaction activity on the catalyst surface. This result leads to decreased composition, yield, and selectivity of FAME and biodiesel with increasing WHSV [20].

In this research, the best FAME yield is 77.19 % achieved at WHSV of 1.186 min^{-1} and residence time or time on stream of 1.25 min. As a comparison, Istadi et al. [14] studied biodiesel synthesis with the same catalyst (but without plasma) in the batch reactor system. The latest conventional process required 4 h reaction time to obtain 74.52 % yield of FAME which is lower than that with the presence of plasma role. This results proved that the catalytic-plasma reactor system is promising due to producing a higher yield of FAME or biodiesel in a short reaction time which is stated as significant improvement in this research.

Effect of catalyst diameter on performance of the catalytic-plasma reactor

The effect of catalyst diameter on yields of FAME and biodiesel was presented in Figure 7. The figure shows the optimum FAME yield of 77.19 % at a catalyst diameter of 5 mm over the transesterification process over the hybrid catalytic-plasma reactor. As a comparison, researches conducted by Marlinda et al. [21] and Chen et al. [22] indicate the similar trend. Marlinda et al. [21] studied the effect of catalyst particle diameter on biodiesel production by the ultrasonic-assisted process. The catalysts used in the research were banana stem ash and coal fly ash with diameter of 100 mesh. Chen et al. [22] investigated the effect of catalyst size at NO_x removal on non-thermal plasma catalyst. They reported that the catalyst particle size affects chemical reactions of gas-solid phase, internal and external diffusion of gas. The catalyst particle diameter also affects removal efficiency of NO_x. Increasing the catalyst size that resulted in increased NO_x removal efficiency, then decreased in the same pattern.

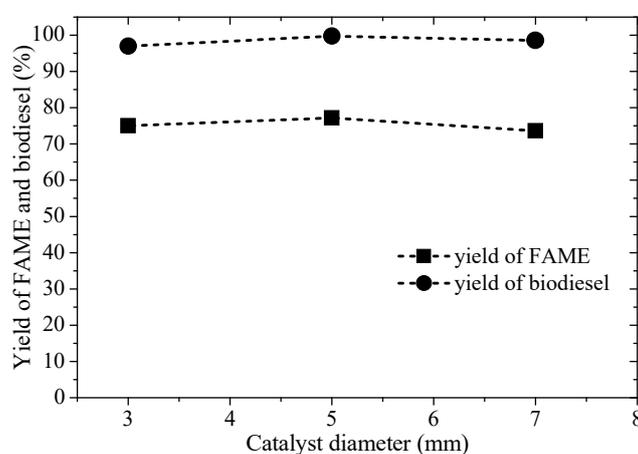


Figure 7. Effect of catalyst diameter on the FAME yield in a hybrid catalytic-plasma reactor using 5KCZ catalyst ($WHSV=1.186 \text{ min}^{-1}$; $CaO:ZnO=3:1$; $V=5 \text{ kV}$)

In this research, the yield of FAME increased with catalyst diameter, but decreased after. Optimum diameter catalyst (d_{opt}) was found to be 5 mm that gives a maximum yield of FAME. In the catalytic-plasma process, active species that consist of free radicals and metastable compounds were generated within the plasma discharge zone and catalyst pores. When the catalyst diameter is smaller than the optimum catalyst diameter ($d_p < d_{opt}$), the transesterification reaction only occurs predominantly on the surface of catalyst without adsorption-desorption process within internal pores of the catalyst. Also, at smaller catalyst diameter, the void fraction becomes lower within the catalyst leading to a decreased FAME yield. The larger the catalyst diameter, the larger void fraction in the catalyst, so that the discharge gap becomes wider and eventually discharge volume increases leading to the increased yield of FAME. When the catalyst diameter was larger than the optimum diameter ($d_p > d_{opt}$), the yield of FAME declined slightly due to a decreased discharge power [23] which is energy used by the plasma reactor to occur the excitation, dissociation, or even ionization processes of reactant molecules. Also, increasing the catalyst particle size decreases the reaction rate which may be due to the smaller external surface area of the catalyst and enhanced diffusion

resistance for triglyceride from the bulk liquid phase to that surface [24]. Finally, the fewer number of excited reactant molecules lead to a declined yield of FAME.

Effect of catalyst basicity on the transesterification process

The catalyst basicity predominantly influences the activity of catalytic transesterification reaction. The higher the catalyst basicity, the higher the catalytic activity tailoring the conversion of triglyceride [24, 25]. Calcium oxide (CaO), known as high basic strength catalyst, has a weakness on the transesterification process, i.e., leached by methanol and small surface area as reported by Taufiq-Yap et al. [16]. In some researches, supported calcium could prevent the leaching by methanol that inhibits the catalytic activity during biodiesel production [26]. Usually, the catalyst support, as a porous material, could also increase the surface area [24]. The catalyst support, such as zinc oxide (ZnO), is inexpensive, stable, reusable, available commercially, and environmentally benign [26] and is potential to be used. The basicity of the catalyst could also be increased with the dispersion of CaO on the ZnO surface [24]. However, as compared to pure metal oxides (CaO or ZnO), a mixed metal oxides (CaO-ZnO) gives stronger basic strength on the catalytic site of catalysts as well as increased the catalyst surface area. The zinc oxide generates strong basic sites that providing a strong interaction between CaO and ZnO. It leads to the electron transfer from metal zinc oxide support interface to CaO as reported by Taufiq-Yap et al. [16].

Improving the catalyst basicity could also be done by impregnating with alkaline components. When the zinc oxide was impregnated by alkaline oxides, the activity substantially increased [26]. In this research, the CaO-ZnO mixed metal oxide was impregnated by potassium nitrate (KNO_3) to improve the catalyst basicity instead of the decreased basicity due to the presence of ZnO component and the leached CaO content by methanol [15]. The impregnated KNO_3 or K_2O on the CaO-ZnO catalyst also has a role as a binding agent to enhance the mechanical strength of the catalyst without significant decreased of basicity.

Concerning performance comparison of fresh and spent catalysts on the FAME yield was presented in Table 4 with respect to effect of catalyst basicity. Table 4 shows that the higher catalyst basicity produces the higher yield of FAME because the catalytic activity of the catalysts is mainly dependent on their basicity. The FAME yield of the transesterification process achieved 75.58 % and 77.19 % when using CaO-ZnO and 5KCZ catalysts, respectively. From the results, activity and selectivity of the 5KCZ catalyst increased with the addition of K_2O as a promoter which was also reported previously by Istadi et al. [14]. This result implies that the catalyst basicity has a significant effect on their catalytic activities. The K_2O doping enhances the number of base active sites in addition to role as a binder of the catalyst to improve the mechanical strength. The more number of the basic sites, the higher the activity of the catalysts, so that the reaction activity is also enhanced [24, 27].

Table 4. Effect of catalyst basicity on yield of FAME

Catalyst	Basicity [$\text{mmol}\cdot\text{g}^{-1}$]	Yield of FAME [%]
CaO-ZnO	0.662	75.58
5KCZ (fresh)	1.090	77.19
5KCZ (spent)	1.00	-

Table 4 also indicates a decreased catalyst basicity of 5KCZ after the transesterification process (spent catalyst). The similar characterization results are also shown in the XRD pattern (Figure 2). The intensity peak of K_2O slightly decreases after used in the transesterification process due to leached by methanol during the transesterification reaction. The decrease of basicity was mainly due to the CaO leaching by methanol rather than K_2O loss.

In the catalytic plasma reactor system, the catalyst basicity has a significant effect on the transesterification process which affects the catalytic activity. The higher the catalyst basicity, the more the basic active sites, so that more adsorbed reactants on the catalyst surface. In the plasma reactor, the high-energetic electrons from electrode collide with molecules of the reactant on the catalyst surface to produce active species which easily react with adsorbed reactants on the surface of the catalyst leading to high selectivity to FAME or biodiesel product rather than a degradation process by the electrons. This phenomenon indicates the synergistic roles of catalyst basicity and plasma reactor system. The synergistic roles lead to enhanced reaction activity and increased reactant conversions, and finally shortened the length of reaction time significantly.

Effect of plasma environment on performance of the catalytic-plasma reactor

Table 5 presents effect of plasma implementation on the yield of FAME. Plasma has a significant impact on the transesterification process. The FAME yield achieved 49.75 % and 77.19 % by the transesterification process without and with plasma roles, respectively. In conventional heterogeneous catalyst using a catalytic fixed bed reactor (without plasma), the transesterification process needs 1-4 h time on stream. In comparison, de Moura et al. [28] needed 3 h reaction time to produce biodiesel yield of 98.54 %, while Ren et al. [29] required a residence time of 56 min to achieve 95.2 % biodiesel conversion. Another research, the 60 minutes residence time was required by Shibasaki-Kitakawa et al. [30] to acquire 80 % biodiesel conversion in the continuous transesterification process of crude triolein with ethanol in a fixed bed reactor. In this research for a comparison study of a process with plasma and without plasma, the yield of FAME for the catalytic transesterification process without plasma achieved 49.75 % at 1.25 min residence time. Meanwhile, the transesterification process with plasma (but without catalyst) resulted in 75.65 % of FAME yield at 2 minutes residence time [7]. In this paper, the proposed novel method (hybrid catalytic-plasma transesterification process) shows better performance with 77.19 % FAME yield at 1.25 residence time (reaction temperature of 65 °C, reactor pressure of 1 atm, alcohol/oil molar ratio of 15:1, catalyst diameter of 5 mm, and WHSV of 1.186 min^{-1}). This result indicates that the synergistic roles of plasma and catalysis lead to improved reactant conversions and higher selectivity to the desired products.

Table 5. Effect of plasma environment on the transesterification process

Treatment	Yield of FAME [%]	Reaction time [min]
Catalytic transesterification without plasma	49.75	1.25
Catalytic transesterification with plasma (hybrid)	77.19	1.25
Transesterification with plasma (without catalyst) ^a	75.65	2.00

^aIstadi et al. [7]

On the plasma-assisted transesterification process, there was a synergistic effect between the high energetic electrons from plasma role and the heterogeneous catalyst surface. The high applied voltage on the electrode has a role in providing high enough energy to the electrons flows from high voltage electrode to ground electrode and can interfere (excite) the electron pairs of covalent bonding of the reactant molecules within discharge zone. The catalysts play a role in improving the selectivity of formation of fatty acid methyl ester products and controlling reaction mechanism within plasma discharge zone. The contact between the catalyst and the high energetic electrons would generate reactive species, such as excited atoms, free radicals, molecules and ions within plasma discharge zone and pores of the catalyst so that would increase reaction activity between the adsorbed reactants on the catalyst surface and the active species [9, 19]. The high energetic electrons collided with reactants molecules, forming highly reactive species, then would interfere the electrons pairs from covalent bonding of the reactant to vibrated, excited, dissociated, ionized, even broken the carbon to carbon bond in triglycerides which in turn forms FAME product [7, 9, 10].

CONCLUSIONS

Synthesis of biodiesel on a hybrid catalytic-plasma reactor over 5 % K₂O/CaO-ZnO (5KCZ) catalyst was studied. The results demonstrated that synergistic effects of the plasma system and the catalyst basicity has a significant role on the performance of catalytic-plasma reactor for biodiesel production. It was also proved that adding K₂O as a promoter on CaO-ZnO catalyst would enhance basicity and improved activity, selectivity, and yield of FAME over the 5 % K₂O/CaO-ZnO catalyst, as well as took a role as binding agent to enhance the mechanical strength of the catalyst. The FAME yield achieved 77.19 % when produced by the plasma-catalytic reactor system at an applied voltage of 5 kV, WHSV of 1.186 min⁻¹, and catalyst diameter of 5 mm. The catalytic-plasma reactor was considered as a promising method due to producing a high yield of FAME or biodiesel in a short reaction time. The synergistic roles of plasma and catalysis led to improved reactant conversions and higher selectivity to the desired products.

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