Effect of Catalyst Pellet-Diameter and Basicity on Transesterification of Soybean Oil into Biodiesel using $K_2O/CaO-ZnO$ Catalyst over Hybrid Catalytic-Plasma Reactor

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Abstract. This research is aimed to study the effect of catalyst pellet-diameter and catalyst basicity on the transesterification process of soybean oil into biodiesel over a hybrid catalytic-plasma reactor. Various catalyst diameters (3, 5, and 7 mm) were tested in this reaction system. Catalyst basicity was also examined by comparing fresh and used catalyst as well as with and without K_2O promoter. All catalysts testing were performed in a hybrid plasma-catalytic reactor (dielectric barrier discharge – DBD type). From the results, the synergistic effects roles of the catalyst and the plasma in the transesterification process are important, in which the energetic electrons within plasma assist the reaction on the catalyst surface by an exciting bonded electron. The catalyst basicity was influenced by the composition of CaO on the catalyst as well as roles of the alkaline K_2O promoter. Catalyst basicity is important in producing biodiesel with high performance. Yield of fatty acid alkyl ester (FAAE) or biodiesel is slightly influenced by the catalyst diameter within the range of diameter studied.

Keywords: biodiesel; catalyst pellet-diameter; DBD plasma reactor; $K_2O/CaO-ZnO$ catalyst

1 Introduction

Currently, energy consumption is increasing as economic and population growth globally. Fossil energy as a non-renewable energy source is the world's major energy source. The serious problem faced by developing countries is the limited fossil fuel, while the need for fossil fuels is increasing [1], resulting in an energy crisis. To overcome the energy crisis and to support the government programs to achieve national energy security, the alternatives to fossil fuel sources from renewable fuel sources are needed. One of the energy alternatives is biodiesel which is consisting of fatty acid alkyl ester (FAAE), biodegradable, non-toxic, and has low emissions [2].

Conventionally, biodiesel was produced by transesterification of triglyceride from vegetable oils or animal fats with alcohols using a homogeneous or a heterogeneous catalyst. The heterogeneous catalyst can be used several times with easier end product separation, can be recycled, minimize costs of raw material and production, more environmentally friendly, and can be applied to batch or continuous processes without the need of purification [3-4]. However, the homogeneous catalysts were more widely used due to high conversion and fast reaction. The heterogeneous catalysts can simplify the production process and refining processes, reduce the amount of waste water, reduce the size of

process equipment, reduce environmental problems and process costs [4].

Among the alkaline earth metal oxides, CaO is the most heterogeneous base catalyst used for transesterification due to capable of producing 98% FAME yield in the first reaction cycle [6], but it needs longer reaction time than the homogeneous one. ZnO is more commonly used in the transesterification process, because it exhibits a good yield of biodiesel [7,8]. When the ZnO catalyst was impregnated with alkaline earth metals, it showed good catalyst activity for the soybean oil transesterification process [9]. To increase basicity of the alkaline earth-based heterogeneous catalysts (CaO , BaO , MgO , SrO), a catalyst promoter is required. The alkali metal (Li , Na , or K) can be used as a promoter of the catalyst to increase its basicity by impregnation method [4,10]. The mixed of ZnO and CaO metal oxides prepared with co-precipitation followed by impregnation by alkali oxide (K_2O) may increase the surface area and catalyst basicity [4].

The transesterification process by continuous process is expected due to the following advantages, i.e.: easier reaction control, relatively small space requirements, can be used for large capacity, produce high yield and easy scaling for large-scale production [11]. Some additional technologies were applied in order to enhance the catalytic reactor performance, i.e. microwave irradiation, ultrasonic, electro-catalysis method [12], and a hybrid plasma-catalytic method [4]. The hybrid plasma-catalytic

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process is promising because the high voltage plasma provides high energetic electrons to assist the catalytic process by exciting the bonded electrons of the reactant molecules in the catalyst surface [4,12]. In addition, the presence of a catalyst can increase the contact surface area between the reactant molecules and the high-energetic electrons so that the breakdown of chemical bonds becomes more efficient. Therefore, particle size of the catalyst within discharge zone is important to be studied. This research is aimed to study the effect of catalyst pellet-diameter and basicity of catalyst on the transesterification process of soybean oil into biodiesel over a hybrid catalytic-plasma reactor.

2 Materials and Method

2.1 Materials

This experimental works used HappyTM soybean oil and methanol (Merck, 99.9%) as the raw materials of biodiesel production. K₂O/CaO-ZnO catalyst was used which was prepared from precursors of calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) Merck, 99%), zinc nitrate tetrahydrate (Zn(NO₃)₂·4H₂O) (Merck, 98,5%), potassium nitrate KNO₃ (Merck, 99%), sodium carbonate (Na₂CO₃) (Merck, 99%), and sodium hydroxide (Merck, 99%).

2.2 Preparation of K₂O/CaO-ZnO catalyst

Preparation of 5%wt K₂O/CaO-ZnO catalyst was initiated by the synthesis of CaO-ZnO catalyst using co-precipitation method followed by impregnation of K₂O. The CaO-ZnO catalyst (CaO:ZnO of 3:1 mole ratio) was prepared by dissolving calcium nitrate (Ca(NO₃)₂) 1 M and zinc nitrate (Zn(NO₃)₂) 1 M in distilled water. Further, the solution was dropped wisely by 2 M Na₂CO₃ solution (10 mL/min) and was stirred until a white-gel was formed. The resulted gel was added by 1 M NaOH to adjust the pH to be 10. The mixed gel was stirred for 24 hours at a temperature of 60 °C. The resulting solid was washed several times by aquadest until alkaline free. The filtered solid was dried in a Memmert oven at 110 °C for overnight. The catalyst was then calcined in a Ney Vulcan box furnace at temperature of 800 °C for 3 hours.

The resulted CaO-ZnO catalyst was impregnated by solution of 1 M KNO₃ while stirred for 1 hour. The wet resulted solid was then dried in the Memmert oven at temperature of 110 °C for overnight. Subsequently, the dry solid was calcined in the box furnace at temperature of 300 °C for 5 hours to produce a K₂O/CaO-ZnO catalyst. Thereafter, the catalyst was pelletized to obtained diameter of 3, 5, and 7 mm.

2.3 Catalyst basicity testing

Catalyst basicity was analyzed by titration method according to Tanabe and Yamaguchi method [13]. In this method, the solid catalyst was suspended in benzene and was titrated with benzoic acid. One-half gram of the

catalyst was put into an Erlenmeyer flask. Twenty mL benzene and 1 mL indicator solution (128 mg of bromthymol blue (BTB) in 100 mL of benzene) was poured into the Erlenmeyer flask. The catalyst suspension was indicated by change of 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 suspension 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. (2), where *V* denotes the volume of benzoic acid solution (mL), *N* denotes normality of benzoic acid solution (mgeq.mL⁻¹), and *W* represents a weight of catalyst sample (g) [4].

$$\text{Basicity (mmol. g}^{-1}\text{)} = \frac{(V \times N)_{\text{benzoic acid}}}{W_{\text{catalyst}}} \times 100\% \quad (2)$$

2.4 Catalyst testing for biodiesel production

Experimental rig for 5wt%K₂O/CaO-ZnO catalyst testing in the transesterification process of soybean oil over a hybrid plasma-catalytic reactor (Dielectric Barrier Discharge – DBD type) was depicted in Fig. 1.

Fig. 1. Experimental rig for transesterification process using a hybrid fixed bed plasma-catalytic reactor: (1) methanol tank, (2) oil tank, (3) valve, (4) agitator, (5) board, (6) dosing pump, (7) regulator stirrer, (8) thermostat & controller, (9) mixing tank, (10) high voltage power supply, (11) high voltage probe, (12) multimeter, (13) electrode rod, (14) catalyst pellet, (15) glass tube, (16) heater jacket, (17) container tank, and (18) ground.

The catalytic-plasma reactor consisted of a high voltage (HV) electrode, a ground electrode, glass barrier, and a packed of catalyst bed placed within HV discharge zone. The HV electrode was made of the copper rod with a 0.5 cm in diameter and 30 cm in length placed in the center of reactor tube. The ground electrode was made of stainless steel plate rounded around the HV copper rod with a 3 cm in tube 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 gap between electrodes, a distance between the high voltage electrode and the ground electrode, was 1.27 cm. A packed of catalyst pellet (certain diameters) was placed within a discharge zone.

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. The transesterification process was operated at 7 kV voltage, 65 °C reaction temperature, and 1,186 min⁻¹ WHSV.

Analysis of the reaction products (mainly of FAAE components) was done by using Gas Chromatography-Mass Spectrometry (QP2010S SHIMADZU, DB-1 column). The samples were analyzed by programming the GC as follows: heated up to 50 °C oven temperature (hold for 5 min) and ramped 10 °C.min⁻¹ to 260 °C and held at later temperature for 33 minutes. The yield (%) of FAAE were determined using Eqns. (1).

$$\text{Yield (\%)} = \frac{\rho_{\text{biodiesel}} \times V_{\text{biodiesel}} \times \% \text{FAAE GC Area}}{m_{\text{soybean oil}}} \times 100\% \quad (1)$$

3 Results and Discussion

3.1 Effect of catalyst pellet-diameter on performance of plasma-catalytic process

Production of biodiesel using the hybrid plasma-catalytic process is influenced by synergistic effect between plasma role of DBD reactor and catalytic process with 5wt%K₂O/CaO-ZnO as a solid catalyst. The synergistic effect involves roles of the catalyst and the plasma simultaneously in the transesterification process in which the energetic electrons within plasma assist the reaction on the catalyst surface by exciting bonded electrons.

In the packed bed reactor system within discharge zone, surface area of contact between the energetic electrons and the catalyst surface is important. The intimate contact could be covered when the surface area of catalyst is increased including void fraction of the packed bed. The high void fraction includes void inside catalyst pore and void within packed bed. From Fig. 2, the yield of FAAE is slightly influenced by the catalyst diameter within the range of diameter studied. This means changes of catalyst diameter only slightly affected on reaction performance.

Optimum diameter catalyst was found to be 5 mm that gives a maximum yield of FAAE relatively. 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 diameter, the transesterification reaction only occurs predominantly on the surface of catalyst without

adsorption-desorption process within internal pores of the catalyst. Also, the smaller the catalyst diameter, the smaller void fraction within the catalyst bed, so that the FAAE yield decreased. The larger the catalyst diameter, the larger void fraction in the catalyst, so that discharge void fraction would be increased.

Fig. 2. Effect of catalyst diameter on FAAE yield

3.2 Effect of catalyst basicity on performance of plasma-catalytic process

Basicity of the catalysts (fresh and used) was presented in Table 1. The table indicated an increased basicity due to promoting the CaO-ZnO with K₂O. The high basicity is due to higher basic strength of calcium oxide, and promoted by an impregnation of K₂O. The basicity of the catalyst could also be increased with good dispersion of CaO on the ZnO surface.

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.* [15]. Improving the catalyst basicity could also be done by impregnating with alkaline components as a promoter. In this research, the CaO-ZnO mixed metal oxide was impregnated by potassium nitrate (KNO₃) solution to improve the catalyst basicity as compensation of the basicity decrease due to the presence of ZnO component and the leached CaO content by methanol. From Table 1, the increased basicity of catalyst leads to higher FAAE yield.

Table 1. Effect of basicity of catalyst on FAAE Yield

Catalyst	Basicity (mmol/g)	FAAE yield (%)
CaO-ZnO	0.662	75.58
5%K ₂ O/CaO-ZnO (fresh)	1.090	77.19
5%K ₂ O/CaO-ZnO (used)	1.000	-

3.3 Characterization of FAAE as biodiesel product

Characterization of fatty acid alkyl esters (FAAE) as biodiesel product of the hybrid plasma-catalytic reactor is presented in Table 2. From the table, it can be suggested that the reactor product fulfill the basic specification of biodiesel according to the SNI standards.

The measurement of biodiesel characteristics used ASTM method as stated in Table 2.

Table 2. Characterization of biodiesel product (1: ASTM D 1298; 2: ASTM D 445; 3: ASTM D 664)

Parameter	Biodiesel / FFAE at Various Catalyst Diameter (mm)			SNI Standard	Soybean Raw Material
	3	5	7		
Density (g/mL) ¹	0.88	0.90	0.90	0.85-0.89	0.92
Kinematic Viscosity (40 °C) (mm ² /s) ²	3.84	4.01	4.15	2.3-6.0	8.46
Acid Number (mg KOH/g) ³	0.34	0.34	0.22	< 0.8	0.56
FFA concentration (%) (oleat)	-	-	-	-	0.28 %

4. Conclusion

Production of biodiesel over a hybrid plasma-catalytic process is strongly influenced by a synergistic effect between plasma role of DBD reactor and catalytic process with 5wt%K₂O/CaO-ZnO as a solid catalyst. The synergistic effects involve roles of the surface of catalyst and the plasma in the transesterification process in which the energetic electrons within plasma assist the reaction on the catalyst surface by the exciting bonded electrons. The yield of FFAE as biodiesel product is slightly influenced by the catalyst diameter. In the packed bed reactor system within discharge zone, the surface area of contact between the energetic electrons and the catalyst surface is important. The intimate contact between reactant molecules and the energetic electrons from plasma could be covered when the surface area of the catalyst is increased including the void fraction of the packed bed. The higher catalyst basicity is due to higher basic strength of calcium oxide, and promoted by impregnation of alkaline K₂O. Increased basicity of catalyst leads to higher FFAE or biodiesel product yield.

Acknowledgment

The authors thank to the Directorate General of Research and Development, Ministry of Research, Technology, and Higher Education, the Republic of Indonesia for the financial support received under the research project of Hibah Kompetensi Year 2015-2017.

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