

28-The Effect of Reactant Ratios, Reaction Time and Catalyst Weight Ratios on Production of Biodiesel from Coconut Palm Oil Using Heterogeneous Catalyst

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The Effect of Reactant Ratios, Reaction Time and Catalyst Weight Ratios on Production of Biodiesel from Coconut Palm Oil Using Heterogeneous Catalyst

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Abstract

Development of biodiesel production process is one of the efforts to overcome energy crisis of fuel consumption derived from crude oil, mainly diesel fuel for transportation and industry that increases annually. The crude oil is predicted will diminish within twenty years, therefore vegetable or animal oils are promisingly resource for the production of biodiesel. In the research, biodiesel was produced using CaO as heterogeneous catalyst through transesterification process. The heterogeneous catalyst had more advantages than the homogeneous one since it was not corrosive to metal and polluted to biodiesel and glycerol being produced. The heterogeneous catalyst was easily separated from the liquid product and it could be designed to possess higher activity and selectivity, as well as, longer lifetime.

The aim of the research was to determine the optimum operating condition of the transesterification of coconut palm oil and methanol using CaO as the heterogeneous catalyst to produce biodiesel as main product and glycerol as by product. The process variables included the ratio of coconut palm oil to methanol, $R = 1:6$ ad $1:8$; reaction time, $t = 0,5$ to $3,0$ hours and catalyst weight ratios, $w = 4$ to 12 %. The process was conducted in 500 ml glass reactor completed by agitated heater, thermometer and reflux condenser. Samples were taken at every 0.5 hours, and the glycerol formed and conversion was calculated.

The experimental results showed that conversion of coconut palm oil increased along the reactant ratios, reaction time, and catalyst weight ratios. The reaction rate constant, k increased with the increase of the catalyst weight ratios. The highest conversion of 96.24 % was achieved at reactant ratio of $1:8$, catalyst weight ratio of 12 % and reactant time of 3,0 hours at temperature of 65 °C while the highest k values of $2.16 \times 10^{-2} \text{ min}^{-1}$ was achieved at reactant ratio of $1:6$ and the catalyst weight of 12 %.

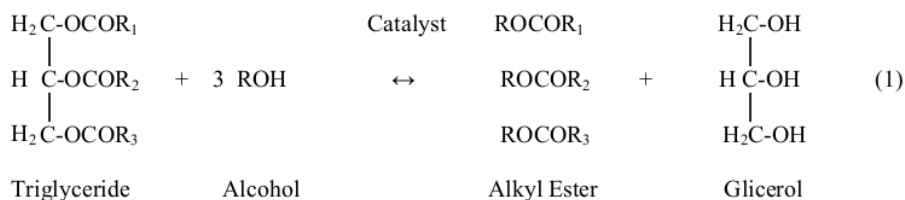
1. Introduction

Usage of fuel oil increases along with its consumption for transportation, industries, power plants, and households. Based on data from Automotive Diesel Oil, the consumption of the fuel oil in Indonesia has exceeded its production since 1995, and it is estimated that the oil stock in Indonesia will diminish within period of 10 to 15 years. The estimation had been proven by lack of fuel oil in some regions in Indonesia. Diversification of energy efforts have been conducted to overcome fuel oil lack in Indonesia. One of the effort is by providing renewable energy resources such as biodiesel. Biodiesel can produced from coconut Plam Oil, Jatropha Curcas Oil, or other vegetable oils, and it is used as alternative for petroleum biodiesel.

Application of vegetable oil for fuel as alternative of diesel oil had been developed by Rudolp Diesel in 1900 in Paris. He created diesel engine by using peanut oil for fuel. Its utilization was left due to low price of crude oil and its viscosity was high approximately 14 times higher than that of diesel oil at 37.8 °C (*PL. Puppung*, 1985). Due to energy crisis in 1973, research of vegetable oil utilization was under interest. Effort to reduce its viscosity was conducted by mixing the vegetable oil with diesel oil, however limited amount of the vegetable oil such as 30 % v of coconut oil was mixed with diesel fuel (*PL.Puppung*, 1986). Pirolisis of the vegetable oil to low chain substances was not economical because it required heat and less liquid product besides forming gas and solid and glycerol formed decomposed to carbon monoxide and ethilen (*Fieser & Fieser*, 1957).

Biodiesel is a name of fatty ester which is commonly known as monoalkyl ester. It is produced from vegetable oils such as Soy Bean oil, Coconut oil, Coconut Palm oil, Corn oil and Jatropha Curcas oil through esterification process (Mardiah et. al. 2006). Biodiesel has molecul formula of $C_{n-1}H_{2(n-r)-1}CO-OCH_3$ with n being even number from 8 to 24 and r : 0, 1, 2 or 3. Several fatty acid methyl ester known are methyl stearate, $C_{17}H_{35}COOCH_3$ [n = 18 ; r = 0], methyl palmitate, $C_{15}H_{31}COOCH_3$ [n = 16 ; r = 0], methyl laurate, $C_{11}H_{23}COOCH_3$ [n = 12 ; r = 0], methyl oleate, $C_{17}H_{33}COOCH_3$ [n = 18 ; r = 1], methyl linoleate, $C_{17}H_{31}COOCH_3$ [n = 18 ; r = 2] and methyl linolenate, $C_{17}H_{29}COOCH_3$ [n = 18 ; r = 3]. Unsaturated fatty acid methyl ester has lower cetana number compared than that of saturated one (r = 0). Cetana number decreases with the increase of number of double chain of the fatty acid methyl ester. Biodiesel can be utilized without mixture of diesel oil or with mixture of diesel oil for vehicles without engine modification. Mixture of 20 % biodiesel and 80 % diesel oil is called B20. B20 used as alternative fuel in United States for bus and truck. B20 reduces emission, low price and it did not require the engine modification (Andi, 2006). Biodiesel is environmental friendly and it is renewable and biodegradable. It has lubricant property to piston, and it has ability to eliminate green house effect, as well as, its stock is sustainable. Biodiesel produces better emission compared to diesel oil, that is: free of sulphur, low smoke number and cetana value from 57 to 62, perfect combustion and it is not toxic.

Transesterification process is utilized to reduce viscosity of vegetable oil and to increase the fuel power to meet standard of diesel oil for vehicles. Methanolysis process to vegetable oil or fat will produce methyl ester and glycerol through breaking triglyceride (*Farris*, 1979). Transesterification process occurs based on the following reaction as in Equation (1):



Several factors affecting the alcoholysis reaction are reaction time, temperature, catalyst, speed of mixing, reactant ratio and concentration. (Raharja and Gunadi, 2000). Higher temperature will accelerate rate of reaction. The effect of temperature on the rate of reaction is affected by catalyst used in the process. The reaction occurs at room temperature with base catalyst, however, it occurs at 100 °C with acid catalyst and at 250 °C without catalyst (Kirk dan Othmer, 1980). Heterogeneous catalyst such as base oxide (SrO, CaO, MgO) can be utilized in the transesterification process. Reaction mechanism for the esterification process using the base oxide catalyst occurs with the following sequence: (1) ion O²⁻ from the base oxide catalyst picks up ion H⁺ from methanol to form methoxide anion; (2) The methoxide anion attaches to the carbonyl carbon from triglyceride to form tetrahedral intermediate; (3) The tetrahedral intermediate picks up ion H⁺ from surface of the base oxide to release the base oxide; (4) The tetrahedral intermediate also reacts with methanol to form methoxide anion; and (5) Tetrahedral intermediate forms biodiesel and glycerol.

Research relating with the alcoholysis of vegetable oil had been conducted by several researchers since 1979. In 1979, Farris performed research regarding with alcoholysis of soybean oil with methanol with 2 % NaOCH₃ catalyst, methanol reactant ratio of 6 to 1, temperature of 110 °C with conversion less than 79 % in 60 minutes. Nouredin and Zhu in 1997 conducted alcoholysis of soybean oil with methanol using H₃PO₄ as catalyst with ratio of reactant of methanol to oil of 6 : 1, catalyst 2 % from oil volume, temperature 70 °C, and produced produced methyl ester with conversion of 68 %. In 1999, Kusmiyati performed alcoholysis of Kapok seed oil with methanol using activated zeolite as catalyst to achieve conversion at 64 % at reactant ratio of methanol to oil of 6 :1, temperature of 130 °C, and reaction time of 60 minutes.

The aims of the research were to conduct transesterification process of coconut palm oil with methanol using CaO as catalyst to produce biodiesel (methyl ester) as renewable energy, to study the effect of reactant ratios (coconut palm oil to methanol), reaction time, and catalyst weight ratios to conversion of the coconut palm oil and to obtain operating condition that gave the highest conversion, and to determine the kinetic rate constant of the process.

2. Experimental Method

Process of biodiesel transesterification from coconut palm oil was conducted at a 500 ml glass reactor equipped with reflux condenser, heating mantle, agitator, temperature measurement and sampling port. Main material used for the process was coconut palm oil, methanol and CaO as catalyst. Other materials utilized were aquadest, KOH, sodium acetate, acetic acetate anhydrid, phenolphthalin and HCl for analysis of coconut palm oil, methyl ester and glycerol. Transesterification process was performed by reacting the coconut palm oil with various of reactant ratios (coconut palm oil to methanol) of 1:6 and 1:8; reaction time of 0.5 to 3.0 hours and catalyst weight ratios of 4 to 12 % in the stirred glass reactor. The reaction occurred in the batch mode at constant temperature of 65 °C.

The transesterification process of the coconut palm oil was initiated with reactant ratio of 1 : 6. The reactor glass was filled with 250 ml feed and it was heated to 65 °C. Catalyst of 4 % of the coconut palm oil weight was mixed with methanol to a beaker glass and it was heated at 45 °C, and its mixture was fed to the reactor. Mixture of coconut palm oil, methanol and catalyst was heated to temperature of 65 °C. Transesterification reaction of the coconut palm oil and methanol occurred at the constant temperature for 3,0 hours. Sample of 15 ml was taken every 0,5 hours, and it was kept in bottle sample and left for 24 hours to form two layers. Glycerol formed in the lower layer, while methyl ester formed in the upper one. Glycerol formed was analysed with acetin method (Griffin, 1955) and conversion was calculated for each glycerol formed. The upper layer (methyl ester) was washed with hot water with temperature of 60°C, and the mixture was fed to funnel to separate the methyl ester. Lower layer was discharged, while the upper one was washed with aquadest to obtain pure methyl ester. Methyl ester was heated at temperature of 100 °C to remove water content.

The transesterification process was repeated for different reactant ratio and catalyst weight ratios.

3. Results and Discussion

Process variables observed in the research were reaction time, catalyst weight ratios and reactant ratios. The conversion of coconut palm oil was affected by these variables. The effect of reaction time on the conversion of coconut palm oil at ratio of coconut palm oil and methanol 1:6 with catalyst ratios 4 %, 8 % and 12 % was shown in Figure 1. The conversion of coconut palm oil increased with the reaction time from 0,5 to 3,0 hours. More reaction time allowed the opportunity for the reactants to hit each other more often so that the conversion increased. At reactant ratio of 1:6 and catalyst weight ratios of 4 % with the increase of reaction time from 0,5 to 3,0 hours, the conversion increased from 18.31 % to 70.17 % and with catalyst weight ratios of 8 % and 12 %, the conversion increased from 26.16 % to 94.69 % and from 27.17 % to 95.44 %, respectively. At reactant ratio of 1:8 and catalyst weight ratios of 4 % with the increase of reaction time from 0,5 to 3,0 hours, the conversion increased from 28.01 % to 84.81 % and with catalyst weight ratios of 8 % and 12 %, the conversion increased from 30.77 % to 90.78 % and from 24.98 % to 96.24 %, respectively.

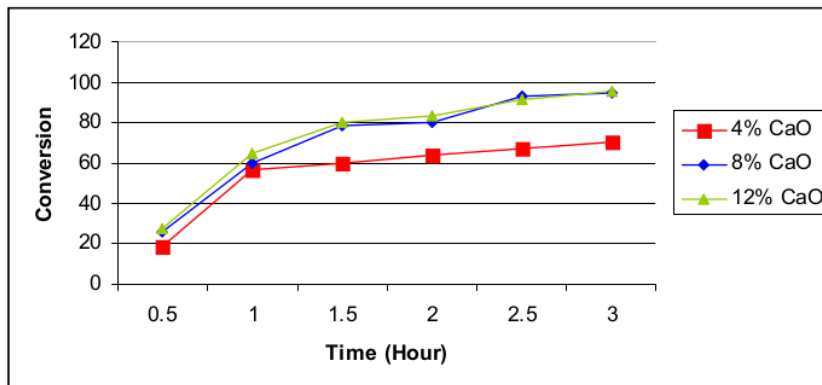


Figure 1. The Effect of Reaction Time to Conversion of Coconut Palm Oil with Ratio of Coconut Palm Oil to Methanol 1:6

CaO catalyst with higher surface area provided higher activity. Addition of catalyst weight ratios enlarged the surface area so that more reactants reacted. Increase of amount of the reacted reactant would increase the conversion of coconut palm oil. Based on stoichiometric of the transesterification reaction, 3 moles of methanol were consumed for each mol of triglyceride to produce 3 molecules of biodiesel and 1 molecule of glycerol. Methanol excess was used to direct reaction equilibrium to the right, that is to direction of biodiesel formation and to increase the conversion of coconut palm oil. Rate of reaction increased with the increase of reactant ratios (coconut palm oil and methanol). As, the reactant ratios increased from 1:6 to 1:8 with catalyst weight ratios 12 % and the reaction time of 3,0 hours, the conversion increase from 95.44 % to 96.24 %.

Reaction kinetics of coconut palm oil and methanol were approached as first order as excess amount of methanol consumed in the reaction. Relation between $-\ln(1-x)$ versus t showed a linear relationship. Kinetic rate constant was obtained as slope of the equation of $-\ln(1-x) = k t$. Values of k were affected by catalyst weight ratios. At reactant ratio of 1:6 and

catalyst weight ratio of 4 %, k value was $6.89 \times 10^{-3} \text{ min}^{-1}$ and it increased from $2.06 \times 10^{-2} \text{ min}^{-1}$ to $2.16 \times 10^{-2} \text{ min}^{-1}$ as the catalyst weight ratio was increased from 8 % to 12 %, respectively.

4. Conclusion

Conversion of coconut palm oil increased with the reaction time, catalyst weight ratios and ratio of reactants. The highest conversion of 96.24 % was achieved at reactant ratio of 1:8, catalyst weight ratio of 12 % and reactant time of 3,0 hours at temperature of 65 °C. Higher reaction time provided more opportunity for the reactants to perform reaction. The highest conversion was achieved with the catalyst weight ratio of 12 % since addition of catalyst caused the increase of reaction area. Excess of methanol increased conversion by shifting the reaction equilibrium to the right. Kinetic rate constant, k increased with the increase of the catalyst weight ratios. The highest k values of $2.16 \times 10^{-2} \text{ min}^{-1}$ was achieved at reactant ratio of 1:6 and the catalyst weight of 12 %.

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