Biodiesel Production from Kapok Seed Oil Using Bimetallic Oxide MgO/CaO as Catalyst in Continuous Fixed Bed Reactor

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Abstract. The study of renewable energy has become increasingly important as scientific research to overcome the increasing consumption for fossil fuel. Biodiesel production in continuous reactor system with heterogeneous catalyst has been pointed out as the solution instead of the conventional method using batch reactor. This study uses non-edible oil kapok seed oil (*Ceiba pentandra*) as the feedstock and MgO/CaO as catalyst. Bimetallic oxide MgO/CaO catalyst with the composition of 10 wt.% of MgO were calcined at 950ºC for 5 h. Degumming process was conducted to separate impurities from kapok seed oil. It was shown that after degumming process the oil has yellow color, brighter than before the pretreatment. It was shown that the FFA value of the feedstock was reached of 22.75%. The esterification process considerably reduced the FFA to 0.7%. The transesterification was maintained in various temperature (60-80ºC) in fixed bed reactor. This work was extended in various reactant flow rate of 20, 30, 40, and 50 mL/min. The highest biodiesel yield of 20.33% was achieved at 70ºC reaction temperature with feed flow rate of 20 mL/min.

Keywords: biodiesel, calcium oxide, fixed bed reactor, kapok seed oil, magnesium oxide, transesterification

1 Introduction

Nowadays, the energy supply from fossil fuel has become important for human activities, especially in transportation sector. Biodiesel has been receiving great attention as one such alternative energy to substitute diesel oil [1]. Its advantages are biodiesel such as biodegradable, non-toxic, and low carbon monoxide emissions [2]. Additionaly, biodiesel can be used in the small amount of diesel oil without impairing the physical-chemical properties, thus, being possible to use in diesel engines without having a need of modification [3].

Biodiesel which can be derived from transesterification between vegetable oil, animal oil, or waste cooking oil and methanol as short-chain alcohol usually called as fatty acid methyl ester (FAME). In the past few decades, palm oil has been potentially used as the main feedstock biodiesel production in Indonesia due to its abundant in production. Palm oil has high demand especially in food industry due to its role as the edible oil. Utilization of palm oil for biodiesel feedstock leads the price of edible oil increased. In adition, high demand of palm oil leads forest clearance on large scale. Biodiesel production derived from non-edible oil have

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great attention which leads many researchers to develop the green method of biodiesel production. The study is needed to overcome the competition in edible oil market [4,5].

Kapok seed oil (*Ceiba pentandra*) as non-edible oil has great potential to be utilized as the feedstock of biodiesel production instead of the edible oil consumption due to its oil containing of 18-40% oil, relatively inexpensive, and its abundant availability in Indonesia [6]. Kapok fiber is also possible to be utilized as the resource for ethanol production due to its contains 35-64% of cellulose content [7].

In typical, biodiesel can be synthesized towards catalyzed transesterification process between long-chain fatty acid and short-chain alcohol with the assistance of homogeneous base or acid catalyst [8]. The disadvantages of homogeneous catalyst utilization leads this type of catalyst is rarely chosen to assist transesterification reaction. Several disadvantages have been reported such as soap formation as the side product and complexity of separation between liquid product and catalyst leading to high energy requirement [2]. Previous studies have been reported the use of heterogeneous catalyst for transesterification which are easily separable in batch system. The use of metal oxide catalyst such as ZnO, SiO, and TiO2/ZrO2 are frequently used to provide the transesterification process, which have been shown to be very interesting [9]. It was reported that metal oxides shows impressive results as catalyst in the methanolysis of soybean oil in batch system, which achieves reactions yield around 90%. The catalyst from alkaline-earth oxides also exhibited good activity in transesterification reaction due to the high basicity. The alkaline-earth oxide has strong potential for application because it serves as less expensive material compared to most of other transition metal. However, magnesium oxide (MgO) exhibits high surface area with low catalytic activity. Introducing of CaO in the mixture of catalyst leads the higher basic strength. Ability of CaO to form the M^{2+}-O^{2-} pair has an important role in transesterification process.

Previous study reported the highest biodiesel yield of 55.22% was achieved at 70ºC for 75 min with kapok seed oil and methanol as the reaction in molar ratio of 1:15. The transesterification was carried out in batch system in the presence of MgO/CaO as catalyst [2]. Few articles reported synthesized of biodiesel in fixed bed continuous system. Its advantages including in low cost of separating catalyst from product mixture, reduction of waste water during the purification of product, and reusability of catalyst. Previous study have been done to study biodiesel production using fixed bed Lewis-bed catalytic system, which results biodiesel yield of 75% using soybean oil and methanol as reactant at temperature of 100ºC. The study reported that slightly higher operating condition is needed in continuous process compared to the batch system [3]. Buasri et. al. (2012) reported that there are several important parameter in obtaining optimum reaction condition for transeterification process such as methanol/oil molar ratio, feed flow rate, catalyst bed height and reaction temperature. Transesterification reaction was carried out in waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor. The highest conversion of 94% was obtained at 60ºC reaction temperature, 8 h residence time, 295 mm packed bed height and 25:1 methanol/oil molar ratio [10].

Utilization of non-edible oil as the feedstock and heterogeneous catalyst may offer less production cost for biodiesel production in large scale. This study aims to develop biodiesel production from kapok seed oil, catalyzed by MgO/CaO bimetallic oxide catalyst in continuous fixed bed reactor. The effects of temperature reaction and feed flow rate were investigated.

2 Materials and Methods

2.1 Materials

The kapok seed oil used was purchased from Pasuruan, Easet Java, Indonesia. Methanol (Bratachem, 98%), MgO (Merck, 99%), CaO (Merck, 99.5%), H_2SO_4 (Merck, 98%), and H_3PO_4 (Merck, 85%) were used without further purification.

2.2 Characterization of kapok seed oil

The fatty acid composition in the kapok seed oil was determined by Gas Chromatography-Mass Spectrometry (GCMS) using GCMS-QP2010S SHIMADZU. Column was packed with SH Rxi 5Sil MS with the length of 30 m and helium as the carrier gas. The initial temperature of oven was adjusted at 50ºC for 5 min and increased by 15ºC min^{-1} to a final oven temperature of 280ºC with the holding time of 19 min. The acid value were determined using titrimetric method [11].

2.3 Degumming Process

Degumming was prepared by heating the kapok seed oil until reaches the temperature of 70ºC. Further, H_3PO_4 solution was introduced into the oil with the amount of 0.1% of oil volume. The degumming process was maintained for 30 min under the temperature of 70ºC. The product and impurities was discarded from the feedstock using separation funnel after 24 h. The remnant solution was heated at 110ºC to remove the remaining water.

2.4 Esterification Process

Esterification was carried out by introducing the oil and methanol in molar ratio of 1:6 followed by adding the acid catalyst (H_2SO_4 solution) 0.5% of oil mass. The esterification was maintained at 60ºC for 1.5 hours. The product was washed using warm aquadest followed by heating to remove the remaining water. The free fatty acid (FFA) value of esterification product was determined using titrimetric method [10].

2.5 Preparation of MgO/CaO Catalyst

The catalysts were prepared by adding the distilled water into the mixture of MgO/CaO with the composition of 10 wt.%. The mixture was stirred at room temperature for 3 h. Afterward, the excess water in the mixture was evaporated by heating at 70ºC until turned into pasta. The remnant solid particle were dried using oven for 12 h at the temperature of 110ºC. Furthermore, the catalysts with the pellet form were calcined at 950ºC for 5 h.

2.6 Transesterification Process

Transesterification was performed by reacting the oil and methanol in molar ratio of 1:15 with MgO/CaO catalyst. Transesterification was carried out in continuous fixed bed consisting of feedstock tank, heater, pump, needle valve, flow meter, reactor (35 cm long and 1 cm inner diameter), jacket electric heater, control panel (temperature controller), condenser, and product tank, as shown in Fig. 1. The tubular reactor was partially filled with 1.4 g of pellets catalyst. The initial pre-heating of feed was placed in the initial stage of system before entering the tubular reactor. The flow of feed through the reactor was controlled by needle valve with the assistance of pump as the driving force. The reactor was heated by electric heater placed along the external of tubular reactor. The output flow was cooled and collected in tank.

The transesterification was maintained in various temperature 60, 70 and 80ºC to study the effect of temperature. The reaction extended by varying the feed flow rate of 20, 30, 40,

and 50 mL/min. Biodiesel products were analyzed by GC analysis to determine the FAME content. The GC analysis using GC HP 5890 with the carrier gas was nitrogen. The initial temperature of GC-FID was adjusted at 150°C for 3 min with rise of 7.5°C min^{-1} up to 250°C. The yield % of biodiesel can be defined as follows:

$$\text{Yield of biodiesel (\%)} = \frac{\text{W of actual biodiesel}}{\text{W of oil}} \times 100\% \quad (1)$$

Where W of the actual biodiesel amount is the actual weight of FAME (g) from the experiment and W of oil is the actual weight of kapok seed oil (g).

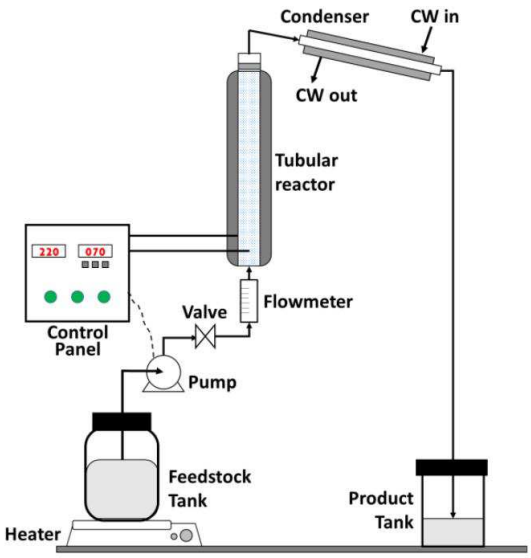

Figure 1. Schematic diagram of a fixed bed reactor apparatus

3 Results and Discussion

3.1 Characterization of Kapok Seed Oil

The composition of kapok seed oil was determined using GCMS analysis. The result shows that kapok seed oil composition are dominated by 9,12-octadecadienoic acid as shown in Table I.

Table 1. Kapok Seed Oil Composition

Component	Value(wt.%)
Pentadecanoic acid	23.98
6-octadecanoic acid	0.59
8-octadecanoic acid	1.16
6-octadecanoic acid	4.01
9,12-octadecadienoic acid	40.18
9-octadecenoic acid	22.31
Octadecanoic acid	3.15
9-octadecynoic acid	1.78
10-octadecenoic acid	1.65
Decane	1.19

Free fatty acid value was determined using titrimetric method [11]. It was confirmed that the FFA value in the feedstock of kapok seed oil is 22.75%. This value is too high for the feedstock before entering the continuous fixed bed reactor. The large amount of FFA leads the saponification reaction [6].

3.2 Pre-treatment Process

Pre-treatment process in this study consisting of degumming process and esterification reaction to prepare the feedstock before entering the fixed bed reactor. The presence of impurities such as gum, latex or oil-slime leads the emulsion of oil and soap so the refining of oil will be hindered [12].

Degumming process was conducted to separate the impurities. Degumming process obtained the white gum layer in the bottom of the oil. The FFA value was also determined after this stage. The FFA value was reduced from 22.75% to 7.55% which can be related to the partially of FFA is settled along with the gum. This value was not suitable for the feedstock due to the previous study reported that the FFA value of kapok seed oil has to be less than 1% for transesterification process [6].

Esterification process aims to reduce the value of FFA in the oil. Esterification was carried out by reacting the oil with methanol in the presence of H_2SO_4 solution as the acid catalyst. Scheme 1 shows the formation of water as the byproduct of esterification process. The FFA of kapok seed oil are converted into fatty acid esters. Based on the result of titrimetric method, it was shown that this process considerably reduced the FFA value to 0.72% which is less than 1%.

$$\underset{\text{(FFA)}}{R_1\text{-COOH}} + \underset{\text{(alcohol)}}{ROH} \xrightarrow{H^+} \underset{\text{(fatty acid ester)}}{R\text{-O-CO-}R_1} + \underset{\text{(water)}}{H_2O}$$

Scheme 1. Esterfication reaction equation

The presence of water as the side product of esterification reaction tends to promotes hydrolysis of triglycerides into FFA due to the saponification reaction [4]. This problem can be overcome by heating the kapok seed oil to remove the remaining water.

3.3 Effect of Temperature Reaction

Biodiesel production was carried out by adding oil and methanol in molar ratio of 1:15. Excess methanol is used to promote the reaction towards the product due to the reversible reaction. Diffusion of reactants on the surface of catalyst also can be facilitated by adding the methanol in larger amount. The larger amount of methanol is applied to overcome the major limitation of mass transfer due to immiscible liquid phases between methanol and oil, also the solid catalyst surface [13].

The pellet catalyst was placed along the inner tubular reactor with the amount of 1.4 g. The effect of reaction temperature was studied in range of 60, 70, and 80ºC. The feed flow rate was held at 30 mL/min.

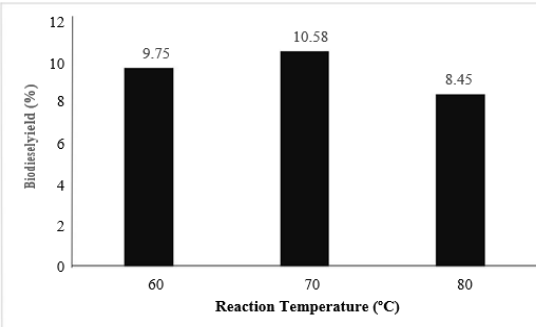

Figure 2. Effect of reaction temperature on biodiesel production at oil to methanol ratio 1:15, 1.4 g MgO/CaO catalyst, flow rate 30 mL/min

Reaction temperature has an important role in kinetic of reaction, which affects the yield of biodiesel. Fig.2 shows that an increase in temperature reaction led to higher yield due to higher rate of reaction. At the temperature of 60ºC, the yield was achiever 9.75%. It can be related to insufficient energy to promote the collision among the reactant [2]. Then, the yield slightly increased due to the increasing of temperature led to collision between the reactant atoms. The higher collision activities will be frequently occurred and sufficient activation energy will be reached in tiny time [8].

The yield decreased to 8.45% by altering the reaction temperature to 80ºC. It can be related to the boiling point of methanol which is around 64.7ºC.When the reaction was maintained at the higher temperature than 70ºC, partially of methanol liquid phase will be turned into vapor phase [13]. The collision between oil and methanol will be less effective occurred in this stage. The methanol molecules have less time to contact on the surface catalyst. The highest yield 10.58% was achieved at 70ºC. Thus, the highest temperature was limited to 70ºC for transesterification of kapok seed oil in fixed bed reactor.

3.4 Effect of Feed Flow Rate

The reaction extended by varying the feed flow rate of 20, 30, 40, and 50 mL/min to determine the optimum operating condition. The feed flow rate has important role to control the residence time of reactant in tubular reactor.

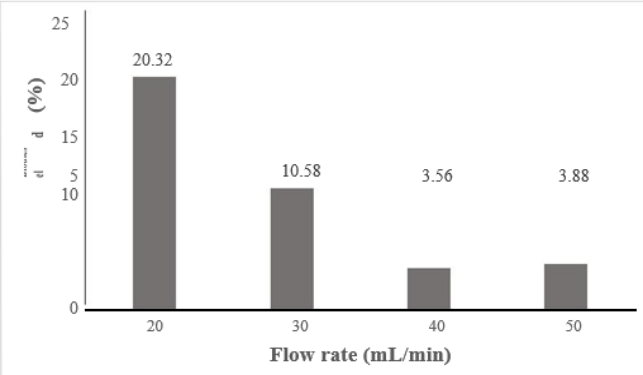

Figure 3. . Effect of feed flow rate on biodiesel production at oil to methanol ratio 1:15, 1.4 g MgO/CaO catalyst, temperature reaction 70ºC

As shown in Fig. 3, the biodiesel yields tend to decreased with the increasing of feed flow rate, as expected. At the low feed flow rate, the highest yield of 20.32% was achieved at 20 mL/min. The effect of feed flow rate is related to the residence time of the reactor. Decreasing of feed flow rate led to a longer reaction time which promote the more active sites contact with reactant. The longer reaction time promote the reaction between kapok seed oil and methanol. Previous study reported that increasing feed flow rate promotes the reduction of mass transfer resistance resulting in high rate reaction. However, too high flow rate of feed led to the reactants pass towards the tubular reactor in a shorter time resulting in a low conversion [13].

4 Conclusion

Biodiesel was synthesized in continuous fixed reactor system with MgO/CaO as heterogeneous catalyst. The effect of parameter including reaction temperature and feed flow rate were found. The highest biodiesel yield of 20.33% was achieved at 70ºC reaction temperature with feed flow rate of 20 mL/min.

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