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RESEARCH ARTICLE

BIODIESEL PRODUCTION FROM KAPOK SEED OIL (CEIBAPENTANDRA) USING MgO/CAO BIMETALLIC OXIDE CATALYST

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ABSTRACT

Biodiesel has been known as the alternative energy which can be used to replace the fossil fuel consumption. Utilization of non-edible oil received much attention due to increasing competition of edible-oil market which leads increasing of the price of edible oil and biodiesel production cost. The common way for biodiesel production is through catalyzed-transesterification, especially heterogeneous catalyzed-transesterification due to its advantages in product separation. This study was conducted using magnesium and calcium oxide as catalyst. Kapok seed oil was used as feedstock for biodiesel production. The catalysts of magnesium oxide/calcium oxide (MgO/CaO) were calcined at 950°C for 5 h. The catalyst were prepared in various composition of MgO (0.5-2 wt.%) to determine the best catalyst composition. The transesterification was maintained in various temperature (50-70°C) and reaction time (30-120 min) in batch reactor. The highest yield of 59.58% was reached for 0.5 wt.% of MgO composition in the catalyst. In the effect of temperature and reaction time study, the optimum condition for biodiesel production was achieved at temperature of 70°C for 75 minutes. Under this condition, the highest biodiesel yield of 55.22% was obtained.

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INTRODUCTION

Development of alternative energy from renewable material research has received much attention due to depletion of fossil fuel reserves and global warming issues. Biodiesel is one such alternative energy which can be used as a substitute for diesel oil (Asri et al., 2013b). In the past few decades, biodiesel has been receiving a great attention due to their advantages, such as biodegradable, non-toxic, and low carbon monoxide emissions (Maceiras et al., 2011). In addition, biodiesel has been considered to replace diesel fuel which can be used in diesel engines without having a need of modification (Asri et al., 2013a). Biodiesel, fatty acid methyl esters, can be derived from vegetable oil, animal oil, or waste cooking oil (Sahar et al., 2018). In Indonesia, palm oil has been considered as the main feedstock of biodiesel production due to its abundance in production. However, palm oil is one such edible oil which has high demand in food industry. Palm oil utilization for biodiesel feedstock leads the price of edible oil increased. Biodiesel production from non-edible oil has been developed by many researchers to overcome the competition in edible-oil market (Lam et al., 2010; Leung et al., 2010). Kapok seed oil (*Ceibapentandra*) has strong potential to be used 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 (Endah Mutiara Marhaeni Putri, 2012). Typically, biodiesel can be produced through catalyzed transesterification process between long-chain fatty acid and short-chain alcohol in the presence of homogeneous base or acid catalyst (Hoekman et al., 2012). However, the use of homogeneous has several disadvantages, such as the formation of soap as byproduct and complexity of separation between product and catalyst leading to high energy requirement. In order to overcome these disadvantages, many studies are concerned in heterogeneous catalyst which are easily separable and reusable (Chouhan et al., 2011). Previous study reported that ZnO, SiO₂, and TiO₂/ZrO₂ catalysts are frequently used to provide the transesterification process (Lamet et al., 2010). It has been studied that alkaline-earth oxides had great performance in biodiesel production due to the higher basicity. The utilization of alkaline-earth oxide also has economical advantages, such as low catalyst cost and long catalyst lifetime. MgO have higher surface area but the catalytic activity is relatively low. The higher basic strength can be achieved by adding the CaO into the mixture of catalyst due to the ability of CaO to form the M²⁺-O²⁻ pair to catalyst transesterification reaction (Sudsakorn et al., 2017). The use of non-edible oil as the feedstock and heterogeneous catalyst may lead to reduction of biodiesel production cost. This study aims to develop biodiesel

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production from kapok seed oil, catalyzed by MgO/CaO bimetallic oxide catalyst. The free fatty acid content in kapok seed oil before and after esterification have been investigated to optimize the transesterification that lead the reaction toward to the biodiesel product. The effects of catalyst composition, temperature, and reaction time were investigated.

MATERIALS AND METHODS

Materials

The kapok seed oil used as the feedstock was purchased from Jepara, Central Java, Indonesia. Analytical grade methanol (Bratachem, 98%), H₂SO₄ (Merck, 98%), H₃PO₄ (Merck, 85%), MgO (Merck, 99%), CaO (Merck, 99.5%), and silica gel blue (Bratachem), were used without further purification.

Characterization of Kapok Seed Oil

The acid value were determined using titrimetric method (Sopianti *et al.*, 2017). The fatty acids profiles that present in the kapok seed oil was detected using Gas chromatography-Mass Spectrometry (GCMS). It consists of HP 6890 with MSD detector and helium as a carrier gas. Column was packed with HP-5MS (5% Phenyl Methyl Siloxane). Initial temperature of front inlet was maintained at 300°C. The starting temperature of oven was maintained at 100°C and increased by 15°C per min to a final oven temperature of 250°C.

Pre-treatment of Kapok Seed Oil

Pre-treatment of kapok seed oil included degumming and esterification process. Degumming was conducted by preparing the kapok seed oil in a beaker glass. The oil was heated and stirred until the temperature reaches 70°C, then 0.1% of oil volume of H₃PO₄ solution was introduced into the oil. This process was maintained for 30 min and left for 24 h after the reaction. Further, the impurities were discarded from the oil using separation funnel. Furthermore, esterification was prepared by introducing the kapok seed oil and methanol in molar ratio of 1:6 followed by adding the H₂SO₄ 1% of oil mass. The temperature was adjusted to desired temperature of 60°C for 1.5 h. The excess water in the oil was remove using silica gel blue. Afterwards, the product of esterification used as the feedstock for the transesterification process. The initial fatty acid methyl ester (FAME) content was determined using Gas Chromatography analysis.

Preparation of MgO/CaO Bimetallic Oxide Catalyst

The catalysts were prepared in various composition of 0.5, 1, 1.5, and 2 wt.% of MgO. Typically, 70 mL of distilled water was introduced into the mixture for each 20 g of CaO. The mixture was stirred for 3 h at room temperature with the speed of 300 rpm. The excess water was evaporated by heating at temperature of 70°C. The remnant solid particle was dried at 110°C for 12 h. Furthermore, the catalyst were calcined at 950°C for 5 h. The surface area of catalyst pores was determine using The Brunauer-Emmett-Teller (BET) method (Naderi, 2015). The metal oxide content of catalyst was confirmed using X-ray diffraction (XRD) analysis. XRD pattern was recorded on a Philips XRD X-Pert XMS using Cu K α radiation, operating at 40 kV and 30 mA.

Catalyzed Transesterification of Kapok Seed Oil

Transesterification was carried out in batch reactor equipped with reflux condenser. The oil and methanol were introduced into the reactor in the molar ratio of 1:15 with 5% MgO/CaO catalyst of the oil mass. The reaction was held at temperature of 65°C for 1.5 h. The best catalyst composition was determined by investigating the yield of biodiesel. Afterwards, the best catalyst composition will be used to determine the optimum condition of biodiesel production. The transesterification was maintained in various temperature of 50, 60, and 70°C for 60 minutes. The reaction extended by varying the reaction time of 30, 60, 75, 90, 120 minutes to study the effect of different operating condition. Biodiesel products were analyzed by Gas Chromatography (GC) analysis using GC HP 5890 with the carrier gas was nitrogen. The temperature of GC-FID oven was adjusted at 125°C for 3 min with rise of 15°C min⁻¹ up to 275°C. The yield % of biodiesel can be defined as follows:

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

Where W of the actual biodiesel amount is the actual weight of FAME (g) from the experiment. Additionally, W of oil is the actual weight of kapok seed oil (g) used in the experiment.

RESULTS AND DISCUSSION

Characteristic of Unreacted Kapok Seed Oil

The kapok seed oil is clear yellow in color. The gas-chromatography and mass spectrometry (GC-MS) was conducted to analyze the kapok seed oil composition. The fatty acid composition of kapok seed oil are given in Table 1, which shows the oil consist mainly of linoleic acid, palmitic acid, and stearic acid. In pre-treatment stage, esterification process was conducted to reduce the levels of free fatty acid (FFA) in the oil by converting the FFA into fatty acid esters. Decreasing FFA leads the reducing soap formation.

Table 1. Fatty acid composition of kapok seed oil (*Ceibapentandra*)

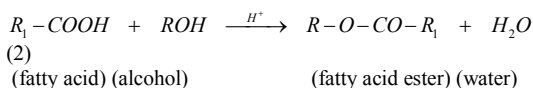
Fatty acid	Value (%)
Caprylic acid	0.10
Nonanoic acid	0.08
Capric acid	0.08
Lauric acid	0.65
Myristic acid	0.37
Oleic acid	0.26
14-pentadecenoic acid	0.18
Palmitic acid	28.51
Heptadecanoic acid	1.08
Linoleic acid	59.10
Stearic acid	9.57

Kapok seed oil shows sufficiently high value of FFA. Its initial FFA value was determined as 1.807%. Previous study reported that FFA in kapok seed oil contains mainly of oleic acid (Sivakumar *et al.*, 2013). The FFA value of kapok seed oil has to be less than 1% for transesterification process (Endah Mutiara Marhaeni Putri, 2012).

Pre-treatment Process of Kapok Seed Oil

Transesterification process will be interfered due to the presence of gum and other impurities, such as latex and oil-

slime (Santoso *et al.*, 2012). Degumming process was introduced to separate the impurities from the oil. White gum on the bottom layer of oil can be eliminated after the degumming process finished. Further pre-treatment step called esterification aims to reduce the level of FFA. Esterification involves the reaction between oil and methanol in the presence of H_2SO_4 as the acid catalyst. Esterification process successfully reduced the FFA value from 1.807% to 0.225%. The value was sufficient to prepare the kapok seed oil for further biodiesel production.



The use of H_2SO_4 solution as the catalyst leads the transesterification occurred simultaneously. The acid catalyst should be eliminated from the product by washing with distilled water. Esterification process also obtains water molecules as shown in Equation (2). The presence of water leads the hydrolysis of triglycerides into FFA due to saponification reaction (Leunget al., 2010). In addition, the water brings the product become very viscous due to moisture-sensitivity of MgO. The water molecule can be removed from the oil by soaking the silica gel blue into kapok seed oil. It was found that 1.90% wt. of FAME was obtained after esterification process finished.

Effect of Catalyst Composition

The effect of catalyst composition was studied by varying the composition of 0.5, 1, 1.5, and 2 wt.% of MgO. The batch reactor was charged with the mixture of oil and methanol in molar ratio of 1:15. Meanwhile, the other conditions were kept constant at 65°C, 1.5 h and 2% of reaction temperature, reaction time and amount of catalyst, respectively. Xie *et al.* reported that the optimum molar ratio of soybean oil to methanol with heterogeneous catalyzed transesterification was achieved in the molar ratio of 1:15 (Xie *et al.*, 2006). Excess of methanol was added into the system to ensure the reaction towards the products due to the reversible reaction. This adjusted molar ratio was used for further transesterification procedure.

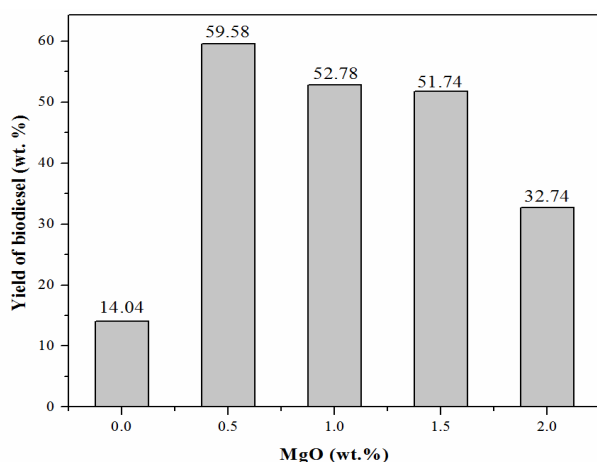


Figure 1. Effect of catalyst composition on yield of biodiesel at oil to methanol molar ratio 1:15, 65°C reaction temperature, 1.5 h reaction time and 600 rpm stirrer speed

In Figure 1, the maximum yield of 59.58% was reached at MgO composition of 0.5 wt.%. It was observed that the yield

increases with increase CaO and decrease of MgO portion in the catalyst. An experiment with the absence of MgO was conducted to study the effect of MgO. The biodiesel yield of 14.04% was achieved at this condition. Previous study reported that the conversion value increases with increase CaO content in the mixture of catalyst in the transesterification of ethyl butyrate with methanol using MgO/CaO. It can be attributed higher concentration of strong basic centers (Albuquerque *et al.*, 2009). Increasing strong basic centers leads methoxy anion formation on the basic centers which has important role for transesterification.

Catalyst Characterization

The metal oxide content and crystallinity of catalyst were confirmed using X-ray diffraction (XRD) analysis. In catalytic activity investigation, the highest yield of 59.58% was achieved at composition MgO of 0.5 wt.%. The XRD pattern of the catalyst with the best composition are presented in Figure 2.

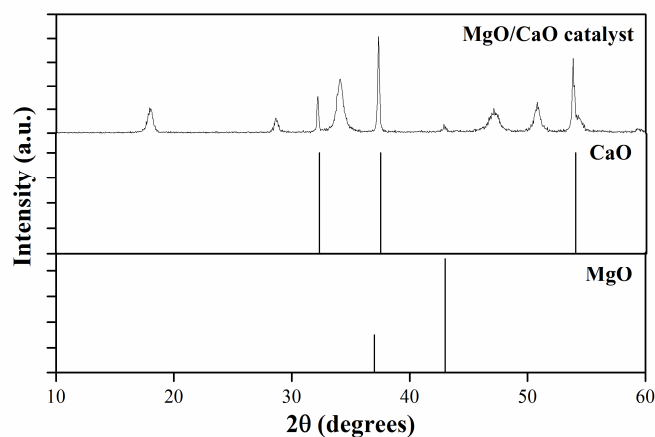


Figure 2. XRD pattern of MgO/CaO catalyst

As seen in Figure 2, the peaks located at 32°, 37°, and 53° can be indicated to peaks of cubic CaO. The weak peak was detected at 43° can be assigned to hexagonal MgO. Other peaks which appeared on the XRD pattern may be attributed to metal carbonates (Albuquerque *et al.*, 2009). Surface area of catalyst pore was determined using BET analysis. It was observed that surface area of MgO/CaO catalyst was 13.319 m²/g.

Effect of Reaction Temperature and Reaction Time on Yield of Biodiesel

Biodiesel production was carried out in batch reactor equipped with reflux condenser. The reaction was performed by adding oil and methanol in molar ratio of 1:15. The catalysts with the composition of 0.5 wt.% were used for this experiment. The catalysts were introduced into the mixture of oil and methanol in the amount of 5 wt.% catalyst of the oil mass. Conventionally, the molar ratio of oil to methanol is 1:6. In this study, excess of methanol is used to increase the yield of biodiesel by shifting the reaction equilibrium towards the product (Asri *et al.*, 2013b). The reaction was extended to study the effect of reaction temperature and reaction time on yield of biodiesel. The effect of reaction temperature was studied by varying the temperature in range of 50, 60, and 70°C. The effect of reaction time was observed at five different reaction time of 30, 60, 75, 90, and 120 min.

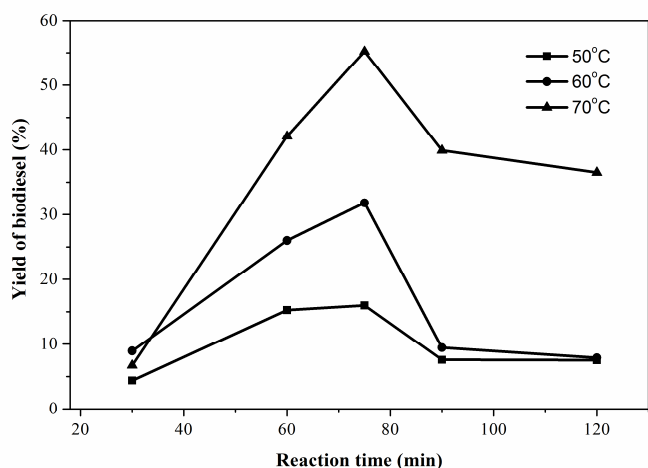


Figure 3. Effect of reaction time on yield of biodiesel at various temperatures at oil to methanol ratio 1:15 and 600 rpm stirrer speed

Figure 3 shows the effect of reaction time at various temperature. Reaction temperature was found to significantly affect the yield of biodiesel. As shown in Figure 3, the reaction occurred slowly at low temperature indicates the reaction rate increases with increase of reaction temperature at all reaction time. The highest yield was reached at reaction temperature of 70°C at various reaction time. The reactions run slowly at low temperature due to insufficient energy to provide the collisions between reactant molecules. Increasing of temperature leads the kinetic rate increases which can be attributed to increasing of molecules which has high velocity to bring the collision between reactants. Moreover, the activation energy will be reached in tiny time to start the reaction (Sivakumar *et al.*, 2013). The reactions were extended at this temperature by varying reaction time of 30, 60, 75, 90, and 120 min. Figure 3 shows the yield of biodiesel had low yield tendency in a short reaction time. It can be related to contact time between reactant molecules occurred briefly. The yield was increased when the reaction was carried out at 30, 60, and 75 min at various reaction temperature. However, the yield was decreased when the reaction time was altered for 90 and 120 min. The longer reaction time reduces the yield of biodiesel due to absorption of excess product on the surface of catalyst. Reduction of active surface of catalyst exposed on the system can be related to absorbed product which covered the surface of catalyst (Endah Mutiara Marhaeni Putri, 2012). Previous study reported that the best reaction time for transesterification is less than 90 min. It can be related to the excess reaction time will promotes the reverse reaction toward the reactants and saponification reaction (Leunget al., 2010). In summary, the highest yield of 55.22% was achieved at temperature of 70°C for 75 min.

Conclusion

In this study, biodiesel was produced from kapok seed oil (*Ceibapentandra*) with methanol through catalyzed transesterification using MgO/CaO bimetallic catalyst in a batch reactor. The reaction was carried out in molar ratio oil to methanol of 1:15. The excess of methanol was used to leads the reaction shifting towards the product. The yield increases with increase CaO content in catalyst mixture due to the increasing of strong basic centers. The highest yield was achieved at MgO of 0.5 wt.%, 65°C, for 1.5 h. The reaction

were extended by varying the temperature and reaction time to determine the best operating condition. The highest yield of 55.22% was achieved at temperature of 70°C for 75 min. The yield of biodiesel increases with increase of temperature due to the activation energy can be reached in tiny time. The longer reaction time reduces the active surface of catalyst which covered by excess product. Therefore, the results can be concluded that utilization of kapok seed oil with methanol using MgO/CaO bimetallic oxide has potential to produce the biodiesel.

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