

Utilization of Kapok Seed Oil (*Ceiba pentandra*) for Biodiesel Production using MgO/CaO Bimetallic Oxide Catalysts

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ABSTRACT

The utilization of renewable energy resources received much attention due to the rapid depletion of fossil fuels. The production of biodiesel using homogeneous catalysts has several disadvantages such as complexity of separation process which leads the high production cost. Magnesium and calcium oxide (MgO/CaO) heterogeneous catalysts can be used to overcome these weaknesses. This study uses kapok seed oil (*Ceiba pentandra*) as the feedstock of biodiesel production. MgO/CaO catalysts were calcined at 950°C for 5 hours. The catalyst activities were studied in various composition of MgO (0.5-2 wt.%) to determine the highest activity. The transesterification was carried out in various temperature (50-70°C) in batch reactor. The highest yield was achieved for 0.5 wt.% of MgO composition in the catalyst with the yield of 59.58%. In the effect of temperature and reaction time study, the highest yield of 55.22% was achieved at temperature of 70°C for 75 minutes.

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1. INTRODUCTION

The increasing of population has driven the energy consumption in transportation sector. The utilization of renewable energy resources received much attention due to the rapid depletion of fossil fuels. Recently, biofuel such as biodiesel has been known as the popular alternative fuel which can be used to replace diesel oil in the transportation sector [1].

Vegetable oil has strong potential to be used as the feedstock for biodiesel production. The advantages of vegetable oil utilization can be attributed to large scale production and environmentally friendly. Vegetable oils can be divided into edible oil and non-edible oil. More than 95% of biodiesel feedstock derived from edible oil. The biodiesel product which derived from edible oil can be used directly as alternative fuel to substitute the diesel oil. But, several disadvantages such as the increasing competition in the edible oil market, leads the price of edible oil and biodiesel production costs increased. Additionally, the competition in edible oil market leads the logging of forests for cultivation. These disadvantages have encouraged many researches on biodiesel production from non-edible oil [2].

Biodiesel as the renewable energy sources can be produced by chemical reaction between vegetable oil or animal fat and short chain alcohols, such as methanol, ethanol, or butanol and supported by catalyst, this process is called transesterification. In term of environmental, the use of biodiesel has several advantages such as reducing the carbon dioxide emissions, nontoxic and biodegradable [3]. Previous studies reported that biodiesel product can be derived from vegetable oil, palm oil, *nyamplung* oil, rapeseed oil, waste cooking oil and so on [4]. Kapok seed (*Ceiba pentandra*) has potential to be utilized as the biodiesel feedstock due to sufficiently high oil containing of 18-25% oil. Kapok seeds oil as non-edible oil are relatively inexpensive and easily obtained in Indonesia.

The process of biodiesel production by conventional method generally uses vegetable oil and short-chain alcohol. The reaction provided by acid or base homogeneous catalysts such as H₂SO₄, NaOH, and KOH [5]. Biodiesel production using homogenous catalyst has several disadvantages, which are sensitive to free fatty acids

(FFA), the formation of soaps as the side product, the complexity of products and catalyst separation, and the presence of alkali wastes that require advanced processes and high energy. These disadvantages may lead to the increasing of production cost. Biodiesel production using heterogeneous catalyzed transesterification can be applied to overcome these problems. Previous literatures reported that ZnO, SiO₂, and TiO₂/ZrO₂ catalysts are frequently used to provide the transesterification process [6]. Several advantages of heterogeneous catalysts utilization such as biodiesel product and catalyst can be separated easily, and catalyst can be regenerated and reused. Hopefully production cost of biodiesel can be reduced by applying the heterogeneous system. In this study, we have developed biodiesel production from non-edible oil, kapok seed oil, catalyzed by MgO/CaO bimetallic oxide catalyst. The effects of catalyst composition, temperature, and reaction time were studied to investigate the yield of reaction.

2. RESEARCH METHOD

The production of biodiesel is achieved through two main stages, pre-treatment stage and transesterification process. The pre-treatment stage aims to remove the impurities and reduce the free fatty acid (FFA) from the raw kapok seed oil. The pre-treatment stage consisting of degumming and esterification process. The kapok seed oil was purchased from Jepara, Central Java, Indonesia. All chemicals were purchased from local market without further purification.

2.1. Degumming Process

Degumming was prepared by heating and stirring the kapok seed oil in a beaker glass 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 minutes. The product and impurities was separated using separation funnel after 24 h.

2.2. Esterification Process

Esterification was carried out in three-neck flask by introducing the oil and methanol in molar ratio of 1:6 followed by adding the acid catalyst (H₂SO₄ solution) 1% of oil mass. The esterification was maintained at 60°C for 1.5 hours. The product was purified using silica gel blue to remove the water as the side product. The product of esterification used as the feedstock for the transesterification reaction. The initial fatty acid methyl ester (FAME) content was confirmed using Gas Chromatography (GC) analysis.

2.3. Preparation of MgO/CaO Bimetallic Oxide Catalysts

The bimetallic catalysts of MgO/CaO were prepared with different MgO/CaO composition of 0.5, 1, 1.5, and 2 wt.% of MgO. The distilled water was added into the mixture of MgO/CaO with the certain ratio. The mixture was stirred for 3 h at room temperature. Excess water was evaporated by heating the mixture at 70°C. The remaining solid particles were dried in the oven at 110°C for 12 h. Furthermore, the catalysts were calcined at 950°C for 5 h in a furnace. The Brunauer Emmett Teller (BET) analysis was conducted to determine surface area of catalyst pores. The final metal oxide content of catalyst was confirmed using X-Ray Diffraction (XRD) analysis.

2.4. Transesterification Process

Transesterification was carried out by reacting the oil and methanol in molar ratio of 1:15 with 5% MgO/CaO catalyst of the oil mass in the batch reactor equipped by reflux system. The bimetallic oxide catalysts which are produced from previous step was introduced into the system. The transesterification was maintained at temperature of 65°C for 1.5 h. Furthermore, the best 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 determine the optimum operating condition. Biodiesel products were analyzed by GC analysis to determine the FAME content.

3. RESULTS AND ANALYSIS

3.1. Characterization of Kapok Seed Oil

The kapok seed oil is clear liquid and yellow in color. Based on Gas Chromatography Mass Spectrometry (GCMS) analysis it is known that kapok seed oil composition are dominated by linoleic acid, palmitic acid, and stearic acid as shown in Table 1.

Table 1. Composition of Kapok Seed Oil

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

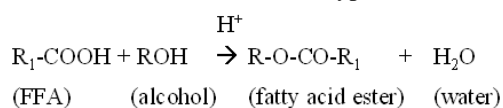
Kapok seed oil shows high value of free fatty acids (FFA). It was found that the FFA content in kapok seed oil feedstock is 1,807%. Previous study reported that kapok seed oil contains mainly FFA as oleic acid [7]. Esterification was placed in pre-treatment stage to reduce levels of free fatty acid (FFA) in the oil by converting the FFA into fatty acid esters. Decreasing of FFA value are expected to reduce the saponification reaction which leads the reaction into the soap formation. For kapok seed oil, the value of FFA has to be less than 1% [8].

3.2. Degumming and Esterification Process

Degumming process aims to separate impurities from cotton seed oil such as latex or oil-slime [8]. The presence of gum leads to the emulsion of soap so that the oil refining process will be interfered. Other impurities such as alkaloids, phosphatides, carotenoids, and others were eliminated by degumming process [9]. Degumming process obtained the white gum on the top layer of oil.

Further pre-treatment stage called esterification aims to reduce the value of FFA in the oil. Esterification was carried out by reacting the oil with methanol in the presence of acid catalyst H_2SO_4 . The FFA of kapok seed oil are converted into fatty acid esters. It was shown that the esterification process considerably reduced the the FFA value from 1.807% to 0.225%. This value was sufficient to prepare 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 [8].

Addition of strong acid solution, H_2SO_4 , as catalyst in esterification process leads the transesterification occurred simultaneously. H_2SO_4 catalysts can be removed from the product by adding the distilled water as the washing agent. Scheme 1 shows the formation of water as the byproduct of esterification process.



Scheme 1. Esterification reaction equation

The presence of water promotes hydrolysis of triglycerides into FFA due to the saponification reaction [6]. In addition, the water content brings the product become very viscous, which could be attributed to moisture-sensitivity of MgO. This problem can be solved by soaking the silica gel blue into the dried kapok seed oil to absorb the excess water. It has been observed that 1.90% wt. of FAME was obtained after esterification process.

3.3. Effect of Catalyst Composition

The effect of catalyst composition was studied to achieve the maximum catalyst activity. The reaction was carried out in batch reactor by adding the oil and methanol in molar ratio of 1:15. Excess methanol is used to ensure the conversion of oil to its esters due to the reversible reaction. Next, catalyst in the amount of 5% of the oil mass was added into the mixture. Transesterification was maintained at 65°C for 1.5 h.

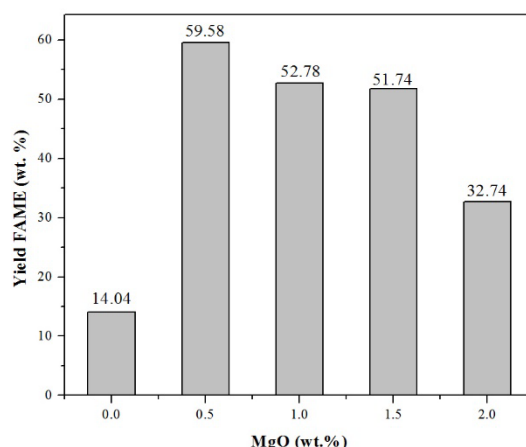


Figure 1. Effect of catalyst composition on biodiesel production at oil to methanol ratio 1:15, 65°C reaction temperature, 1.5 h reaction time and 600 rpm stirrer speed

Figure 1 shows effect of catalyst composition on biodiesel production at oil to methanol ratio of 1:15, 65°C reaction temperature, 1.5 hours reaction time and 600 rpm stirrer speed. In Figure 1, the maximum yield 59.58% was achieved at MgO composition of 0.5 wt.%. The results indicating that yield increases with increase CaO in the mixture of catalyst. For the effect of MgO studies, first we confirmed experimentally that pure CaO reached the yield of 14.04%. Albuquerque et. al. reported transesterification of ethyl butyrate with methanol using MgO/CaO catalyst. Based on their results, the conversion values increases with increase CaO content in the catalysts due to higher concentration of strong basic centres [10]. It can be attributed to increasing of alkalinity leads the protonation of catalyst was easier to form methoxy anion. Methoxide ions from methanol can be generated on these strong basic centers. The methoxide ions which absorbed on the surface of catalyst has an important role for the transesterification. Here we extended the reaction for studying the effect of temperature and reaction time.

3.4. Catalyst Characterization

The maximum yield from the previous experiment was reached at composition MgO of 0.5 wt%, which used for further experiment. The metal oxide content and crystallinity were confirmed using X-Ray Diffraction (XRD).

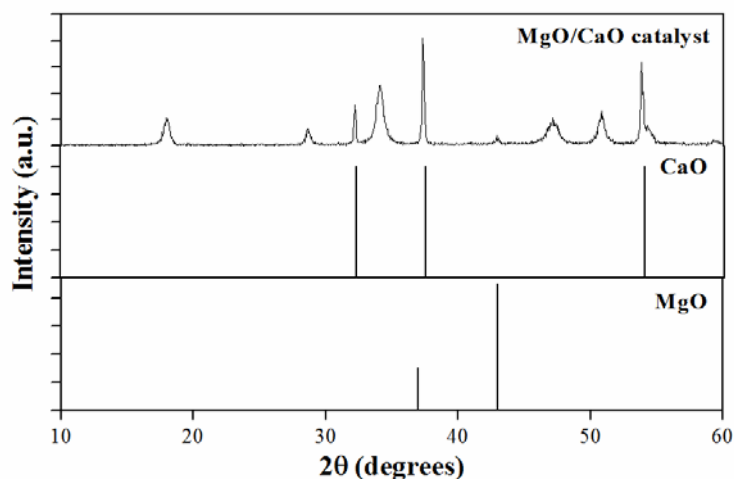


Figure 2. XRD pattern of MgO/CaO catalyst

Figure 2 shows the XRD pattern of MgO/CaO with MgO composition of 0.5 wt.%. The peaks located at 32°, 37°, and 53° can be assigned to peaks of cubic CaO. The weak peak was detected at 43° can be assigned to hexagonal MgO. Other peaks which detected on the XRD pattern may be attributed to metal carbonates [10]. Brunauer Emmett Teller (BET) analysis was conducted to determine surface area of catalyst pore. The value of the BET surface area of MgO/CaO catalyst is 13,319 m²/g.

3.5. Effect of Temperature and Reaction Time

Biodiesel production was carried out by adding oil and methanol in molar ratio of 1:15 into three neck flask. Excess methanol is used to promote the reaction towards the product due to the reversible reaction. The effect of reaction temperature was studied in range of 50, 60, and 70°C. The reaction was held for 60 minutes.

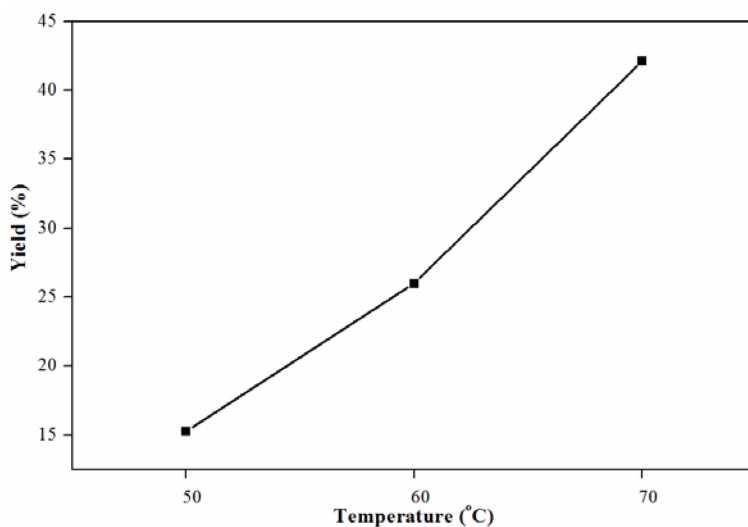


Figure 3. Effect of reaction temperature on biodiesel production at oil to methanol ratio 1:15, 60 min reaction time

Reaction temperature was found to significantly affect the yield of biodiesel. Figure 3 shows reaction occurred slowly at low temperature. The reaction rate increases with increase of reaction temperature. The yield was increased from 15.25, 25.99, and 42.09% when the reaction are carried out at 50, 60, and 70°C, respectively. At lower reaction temperature, there was an insufficient energy to promote the collisions among reactant atoms. As the increasing of temperature, the collision between the reactant particles will be frequently occurred and reached sufficient activation energy [7]. Increasing of reaction temperature leads to the kinetic rate increases due to the increasing of molecules fraction which has high speed and finally promotes the collisions. From these experiments can be determined that the maximum yield was reached at reaction temperature of 70°C. The reaction were extended at this temperature by varying reaction time of 30, 60, 75, 90, and 120 min.

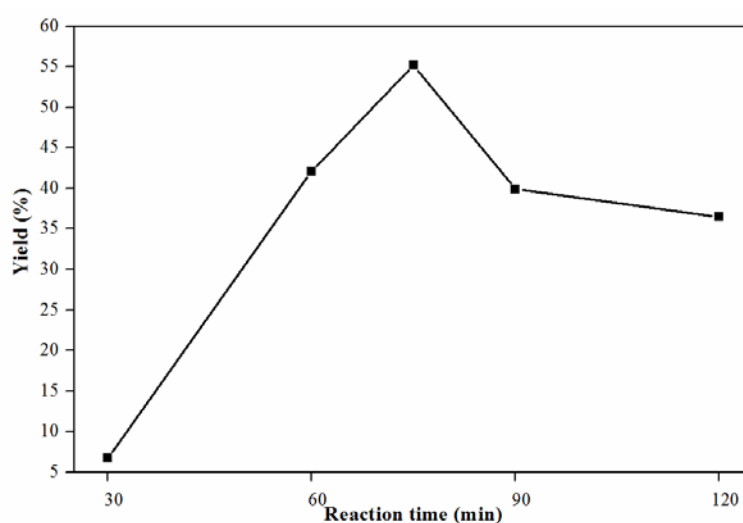


Figure 4. Effect of reaction temperature on biodiesel production at oil to methanol ratio 1:15, 70°C reaction temperature

As shown in Figure 4, the minimum yield was reached at reaction time of 30 min. It can be related to contact time between reactant molecules occurred in tiny time. The yield was increased from 6.71, 42.09, and

55.22% when the reactions were carried out at 30, 60, and 75 min, respectively. However, the yield was decreased from 39.91 to 36.49% when the reaction time were held for 90 and 120 min, respectively. The maximum yield was reached at reaction time of 75 min due to the most of reactant molecules collide each other and reach sufficient energy [7]. When the reaction time altered to 90 min, the yield was decreased to 39.91%. It can be related to absorption of excess product by the catalyst. The reduction of catalyst activity can be related to less active surface of catalyst exposed on the system due to the surface which covered by the absorbed product in longer reaction time [8]. Leung et. al. reported that best reaction time for transesterification is less than 90 min due to the excess reaction time will leads the reverse reaction toward the reactants and saponification reaction [2].

4. CONCLUSION

In summary, we have developed biodiesel production by transesterification of kapok seed oil (*Ceiba pentandra*) with methanol using MgO/CaO bimetallic catalyst in a batch reactor. The effect of MgO presence in the catalyst was investigated to determine the best catalyst composition. The reaction was extended to study the effect of temperature and reaction time. The yield gradually increases with increase CaO in catalyst mixture. The presence of MgO also has an important role to increase the strong basic centres compared to pure CaO. The reaction was carried out in batch reactor with oil and methanol molar ratio of 1:15. The excess methanol is used to promote the reaction towards the product due to the reversible reaction. The maximum yield was achieved at MgO of 0.5 wt.%, 65°C, for 1.5 h. As expected, the reaction rate increased with the increase in reaction temperature which leads the increasing of yield. The maximum yield of 42.09% was reached at 70°C. Furthermore, the experiment at this temperature was extended by varying the reaction time of 30, 60, 75, 90, and 120 min to determine the best operating condition of transesterification for kapok seed oil. The yield is increased with increasing reaction time until achieved the maximum yield of 55.22% at 75 min. The longer reaction time leads the reverse reaction toward the reactants, which can reduce the yield of product. Therefore, it was concluded that transesterification of non-edible oil, kapok seed oil, with methanol using MgO/CaO bimetallic oxide has strong potential to overcome energy issues.

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