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Research Article

Biodiesel Production from *Nyamplung* (*Calophyllum inophyllum*) Oil using Ionic Liquid as A Catalyst and Microwave Heating System

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Abstract

Nyamplung (*Calophyllum inophyllum*) is a typical Indonesian plant. Its seed contains abundant inedible oil, and therefore it is potential for biodiesel feedstock. The current issues of biodiesel are longer reaction time of oil to biodiesel through transesterification reaction and lower biodiesel yield due to ineffective use of a homogenous catalyst. This work was aimed to use an ionic liquid as a catalyst and equipped with microwave heating as the heating system in order to increase the biodiesel yield and accelerate the process. Effects of the catalyst concentration and power of microwave irradiation to the biodiesel yield were studied. The ionic liquid of 1-butyl-3-methylimidazolium hydrogen sulfate ($BMIMHSO_4$) was used as a catalyst. The results showed that the highest biodiesel yield was achieved of 92.81% which was catalyzed by $IL_{0.5}NaOH_{0.5}$ (0.5 wt.% ($BMIMHSO_4$) + 0.5 wt.% NaOH) with a methanol-to-oil molar ratio of 9, a reaction time of 6 minutes, and the microwave temperature was 60 °C.

Keywords: biodiesel; ionic liquid; transesterification; microwave

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1. Introduction

Energy crisis leads to the increase of biodiesel production as a renewable fuel which utilizes vegetable oil as raw material. Biodiesel technologies continue to develop fast esterification and higher obtained yield. Therefore, the process intensification in this area is a very paramount issue. The *nyamplung* (*Calophyllum inophyllum)* is one of the oil contained plants, and its source is abundant in Indonesia. The *nyamplung* seed contains 75% oil, and most of the oil is unsaturated fatty acid [1].

Biodiesel can be produced through a transesterification reaction between triglycerides and methanol using a catalyst in order to enhance the reaction rate. Generally, a base catalyst in the transesterification reaction can be carried out at a lower temperature and has shorter reaction time compared to an acid catalyst [2].

Ionic liquids are a new eco-friendly catalyst which is a type of organic salt composed by

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anions and cations which have a low vapor pressure and as a liquid phase at temperatures below 100 °C [3]. As a catalyst, the ionic liquids has a high catalytic activity, good stability, easily separate from the product, and environmental friendly [4]. The use of the ionic liquid catalyst in the biodiesel production could give more advantages in economic and environmental aspects. In addition, the heating process is required to increase the reaction rate. Microwave as the heating power in the transesterification reaction is more efficient than the conventional heating [5]. The microwave energy can go through to the inside of the material, and the energy is transferred to the material through interfacial polarization mechanism. The mechanism is the combination of dipolar polarization and ion conduction to produce localized and fast heating in the reaction [5]. The conventional heating has some significant drawbacks depend on the material thermal conductivity, specific heat, and heat loss to the environment [6]. Lin *et al.* [6] investigated that the transesterification reaction using the microwave and produced high biodiesel yield of 99.% at a reaction time of 6 minutes.

Elsheikh *et al.* [7] studied three different ionic liquids catalyst, and they are: 1-butylimidazolium hydrogen sulfate, 1-methylimidazolium hydrogen sulfate, and 1-butyl-3-methyl-imidazolium hydrogen sulfate in biodiesel production. Each catalyst activities has been studied toward their reaction of esterification to CPO raw material. The result of the study showed that 1-butyl-3-methyl-imidazolium hydrogen sulfate catalyst activity was better than the other catalysts. Fauzi and Amin [8] have conducted esterification process of oleat acid by using ionic liquid 1-butil-3-methylimidazolium hydrogen sulfate catalyst. The optimal achievement resulted in 81.2% methyl oleic yield on methanol-oleic acid of the molar ratio of 9:1, 0.06 moles of catalyst, 87 °C temperature reaction, and 5.2 h reaction time. Meanwhile, Lin *et al.* [9] also studied the use of 4-alil-4-methylmorpholin-4-ium bromin ([MorMeA][Br]) + NaOH as a catalyst on microwave heating to enhance the methyl ester yield. The highest yield was achieved of 99.4% by using $IL_1NaOH_{0.75}$ (1 wt% [MorMeA][Br] + 0.75 %wt NaOH) catalyst; it was reached on the molar ratio of methanol-to-oil of 9, the reaction time of 6 minutes, and temperature of 70 °C. Lin *et al.* [6] also reported that microwave heating system has better performance than the conventional heating system, faster process, energy efficient and economic. Based on previous studies, the implementation of wave heating and 1-butyl-3-methyl-imidazolium hydrogen sulfate ($BMIMHSO_4$)+NaOH catalyst never been studied. Therefore, the objective of this research is to evaluate the use of microwave heating and an ionic liquid to enhance the transesterification process. The study elaborates the effect of the amount of catalyst and type of catalyst as well as the variation of the power of microwave heating of performance of reaction.

2. Materials and Methods

2.1. Materials

The ionic liquid catalyst of 1 butyl-3-methyl imidazolium hydrogen sulfate ($BMIMHSO_4$) is analytical grade with the purity of 95% and purchased from Sigma-Aldrich. Methanol and sodium hydroxide (NaOH) have the purity of 99.99% and 99%, respectively, and supplied by Merck. Crude of *Calophyllum inophyllum* oil containing 12.8% of FFA was obtained from Kroya, Cilacap, Indonesia.

2.2. Methods

2.2.1. Pre-treatment

Nyamplung oil crude was purified using degumming and neutralization methods to remove the impurities present in the oil. A freshly prepared of phosphate acid 20% with the amount of 0.3% (v/wt) was added into the oil then heated on a hot plate to temperature of 70 °C for 25 minutes. Furthermore, a saturated solution of sodium carbonate with a concentration of 20 mL/100 mL oil was added into the oil then heated at 70 °C for 1 h. Soap and other impurities were separated from the oil by decantation for 24 hours. The oil from decantation result was washed with water at 60-70 °C to obtain the neutral pH of the oil.

2.2.2. Transesterification procedure

The transesterification reaction was conducted in a four-necked batch reactor with a volume of 500 mL equipped with microwave, condenser, temperature sensor, and magnetic stirrer set at 600 rpm. A fixed amount of *nyamplung* oil was placed into the flask, which was preheated to the desired temperatures on a microwave before starting the reaction. The schematic apparatus of the microwave-assisted batch reactor is shown in Figure 1. The transesterification reaction was conducted in a catalyst concentration range of 0.5-1.5 wt%, the oil and methanol molar ratio of 9:1, reaction temperature 60 ^oC and reaction time under microwave heating was 6 minutes. According to Lin *et al.* [6] the best yield of biodiesel was shown at the molar ratio of methanol to oil of 9. The reaction mixture was added into the flask separator until two phases are formed in equilibrium. The upper phase consisted of methyl esters, and the lower phase contained the glycerol. The upper phase samples were taken and injected into Gas Chromatography-Mass Spectrometry (GC-MS) by syringe to determine the concentration of methyl esters. The methyl ester yield (product of methyl ester concentration and biodiesel yield) is defined as follows [6] :

$$\text{Methyl ester yield} = C \, x \, \frac{W_b}{W_{oil}} x 100\ \% \qquad (1)$$

where C: methyl ester content (%); W_b: weight of biodiesel production (g); W_{oil}: weight of the initial amount of nyamplung oil (g).

3. Results and Discussion

3.1. Effect of catalyst concentration in the transesterification reaction using microwave heating

The experiment used NaOH catalyst to study the effect of the catalyst toward the yield. The microwave system was operated at 60 ^oC temperature, the molar ratio of methanol to oil of 9:1 mole/mole, and reaction time of 6 minutes. Catalyst concentration was studied in the range of 0.5-1.5 wt%. As shown in Figure 3, the biodiesel yields were 82.65%, 85.48%, and 84.83% over 0.5 wt% NaOH, 1.0 wt% NaOH, and 1.5 wt% NaOH, respectively. The best yield was achieved of 85.48% by adding 1 %wt NaOH catalyst. Reduction of biodiesel yield was found at 1-1.5% (wt) catalyst. The result showed that over balance of catalyst caused increasing amount of produced glycerol because of saponification occured [6].

The further experiment has been conducted at same amount of catalyst by using NaOH catalyst and $BMIMHSO_4$ ionic liquid (1:1). The microwave system was set at temperature of 60 ^oC, the molar ratio of methanol to oil of 9:1 mole/mole, and reaction time of 6 minutes. Figure 2 shows that the biodiesel yield was 89.69%, 92.81%, and 92.54% of 0.5 wt% $BMIMHSO_4$:NaOH (1:1), 1.0 wt% $BMIMHSO_4$:NaOH (1:1), and 1.5 wt% $BMIMHSO_4$:NaOH (1:1), respectively. The experiment also showed that the best yield was 92.81% with 1.0 wt% $BMIMHSO_4$:NaOH (1:1) catalyst. The result showed that the ionic liquid catalyst could enhance biodiesel yield and increase the use of NaOH catalyst in the amount of 0.5 %wt. The ionic liquid catalyst is soluble in methanol, thereby increasing the contact area between the catalyst and the oil, therefore has a higher rate of reaction [10].

3.2. Effect of [$BMIMHSO_4$]-NaOH catalyst concentration using microwave heating in the transesterification reaction

The experiment was done by varying the catalyst composition of $BMIMHSO_4$ and NaOH on transesterification reaction. The microwave

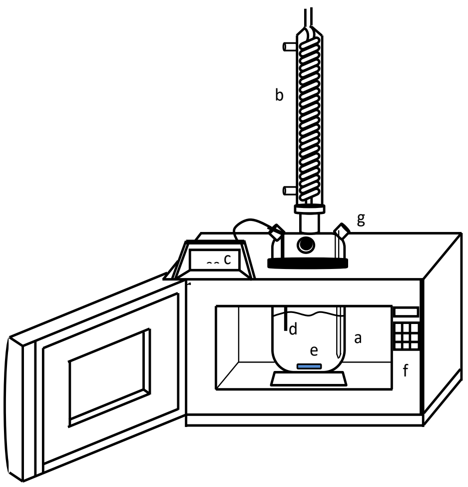

Figure 1. A set of batch reactor with microwave system. a, reactor; b, condenser; c, temperature display; d, temperature sensor; e, magnetic stirrer; f, control panel; g, input raw material

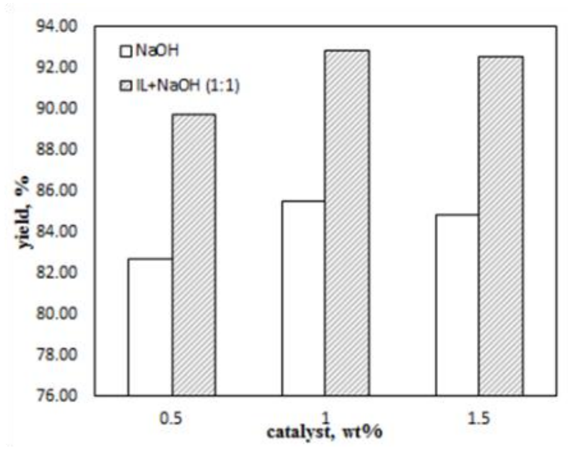

Figure 2. The effect of catalyst concentration to biodiesel yield during the microwave assisted esterification. The catalyst was compared between homogenous catalyst (NaOH) and a mixed catalyst (Ionic Liquid and NaOH at 1:1 vol. ratio) in the range of 0.5-1.5 % (w/w)

was set at temperature of 60 °C, the molar ratio of methanol to oil was 9:1, and time reaction was 6 minutes. The composition of catalyst was varied according to ratio of $BMIMHSO_4$ and NaOH of 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, by adding 1 %wt amount of catalyst composition. Figure 3 shows that the yield increases at $BMIMHSO_4$:NaOH ratio of 3:1, 2:1, and 1:1, but no significant alteration on 1:2, 1:3, and 1:4. The over balance of catalyst has a negative effect on *nyamplung* biodiesel yield due to incomplete transesterification reaction between methanol and oil at shorter reaction time [9]. The best biodiesel yield was 92.81% produced at 1:1 $BMIMHSO_4$:NaOH catalyst composition. Ullah *et al.* [11] reported the reaction mechanism of triglyceride and methanol using the ionic liquid catalyst (Figure 4).

3.3. Effect of system microwave and conventional heating on the biodiesel yield

The effect of the catalyst used in the transesterification reaction using conventional heating was conducted at a constant operation temperature of 60 °C, methanol molar ratio to oil of 9:1, the catalyst concentration of 1 %wt., and reaction time of 180 minutes. Figure 5 shows that the [$BMIMHSO_4$](1)+NaOH(1) 1 wt% catalyst produces higher biodiesel yield (93.99%) better than the use of NaOH 1 wt% (76.29%). The mixed catalyst between [$BMIMHSO_4$] and NaOH have more reactivity compared to the NaOH catalyst because the ionic liquid catalyst has a high catalytic activity and good stability.

The use of the microwave as a heating power in the transesterification reaction using [$BMIMHSO_4$]-NaOH 1 wt% catalyst with a reaction time of 6 minutes can produce 92.81% biodiesel yield, whereas the conventional heating with a reaction time of 180 minutes resulted in 93.99% of biodiesel yield. Figure 3 shows that the use of the mixed catalyst ([$BMIMHSO_4$] and NaOH) gives better results compared with the use of NaOH catalyst. The use of 1 %wt. NaOH catalyst using a microwave at 6 minutes of reaction time obtained 85.48% biodiesel yield, while the use of conventional heating with the reaction time of 180 minutes resulted in 76.29% biodiesel yield. Lin *et al.* [9] reported work on esterification of waste cooking oil (WCO) by microwave system using 4-allyl-4-methylmorpholin-4-ium bromine ([MorMeA][Br])+NaOH ionic liquid catalyst. The highest biodiesel yield was 89.1% by using 1 %wt. ([MorMeA][Br]) + 0.75 %wt NaOH catalyst composition, the molar ratio of methanol to oil of 9, the reaction temperature of 70 °C, and the reaction time of 6 minutes [9]. In addition, Yuan *et al.* [12] studied the effect of the microwave system and conventional heating toward biodiesel yield by used of H_2SO_4/C catalyst, the molar ratio of methanol:castor oil of 12, and the reaction temperature of 55 °C. The reaction reached the balance after 60 minutes of 94% yields with microwave system, meanwhile, with conventional

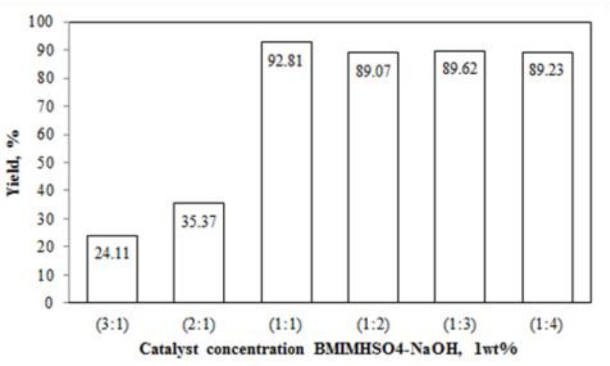

Figure 3. The effect of volume ratio of mixed catalyst (Ionic liquid and NaOH) to biodiesel yield during microwave assisted esterification. The mixed catalyst was varied at 1% (w/w) concentration in the mixture

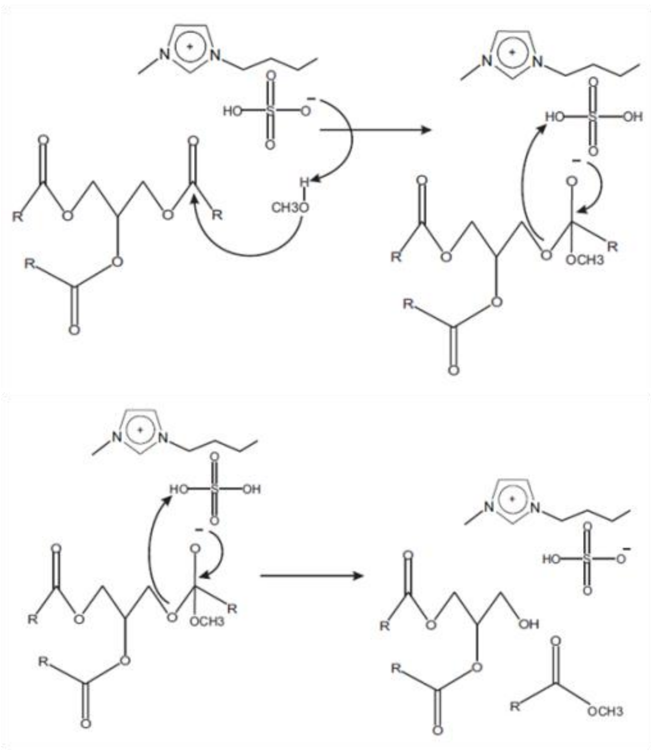

Figure 4. The reaction mechanism of triglyceride and methanol using the ionic liquid [BMIMHSO4] as catalyst [11]

heating, the reaction reach the balance after 180 minutes of 70% yields. The reaction between methanol and oil were getting better because it was exposed by the microwave and then enhance the reaction.

Methanol is one of alcohol that consists of polar compounds [13] which interact to adsorb the microwave, while the nonpolar molecule is an inert [14]. Microwave radiation can increase the chemical reaction due to its capability to deliver the energy directly to the reactant so that the energy transfer is more effective than the conventional heating [15].

4. Conclusions

The result of the study showed that [$BMIMHSO_4$] could increase *nyamplung* bio-diesel yield and reduce the use of NaOH 0.5 %wt catalyst. The best yield was produced at NaOH 1%wt catalyst, the methanol molar ratio to oil of 9, the reaction time of 6 minutes, and the microwave temperature of 60 ^oC. Meanwhile for the $BMIMHSO_4$(1):NaOH(1) 1%wt catalyst, the best yield was achieved of 92.81% with molar ratio of methanol to oil of 9, the reaction time of 6 minutes, and the microwave temperature of 60 ^oC. There were no significant differences in yield by variation of mixed catalyst (ionic liquid: NaOH) at 1:2,1:3 and 1:4 . This concluded that by increasing NaOH in mixed catalyst will not give any improvements of reaction. The conventional heating system resulted in a yield of 93.99% by using the mixed catalyst of $BMIMHSO_4$:NaOH, while the homogenous catalyst (NaOH) only gained 72.69 % yield at process condition of 1%-wt catalyst and 60 ^oC reaction temperature. Furthermore, the used of microwave heating make the transesterification reaction faster than the use of conventional heating. The use of the mixed [$BMIMHSO_4$]+NaOH catalyst and the microwave can be a promising catalyst and heater in the transesterification reaction.

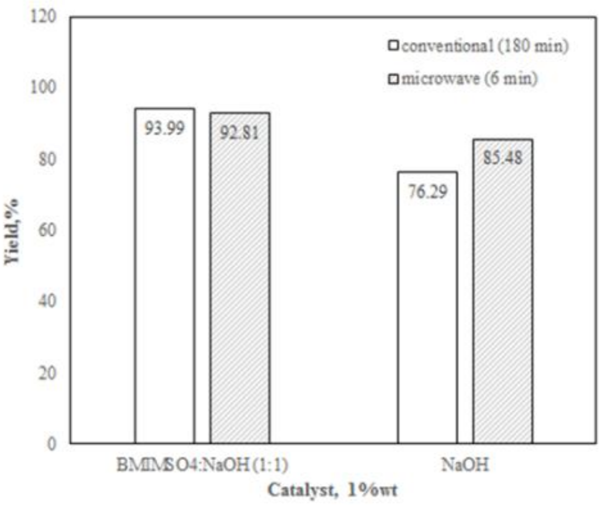

Figure 5. Effect of microwave and conventional heating in the transesterifiation reaction of the biodiesel yield

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