



## Esterification of Nyamplung (*Calophyllum inophyllum*) Oil with Ionic Liquid Catalyst of BMIMHSO<sub>4</sub> and Microwaves-Assisted

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### Abstract

Nyamplung (*Calophyllum inophyllum*) oil contains high free fatty acid (FFA) that is 21.62%. *Nyamplung* oil can be utilized as raw material for biodiesel production. Microwave is a method of heating that is used intensively to speed up the production process. Ionic liquid has high catalytic activity, high selectivity, can be recycled and environmentally friendly. This study learned about the esterification of *nyamplung* oil with ionic liquid 1-Butyl-3-methylimidazolium hydrogen sulphate (BMIMHSO<sub>4</sub>) as catalyst and microwave-assisted. The purpose of this study is to obtain optimum condition of esterification process, with free fatty acid concentration (FFA) <2%. This study uses raw materials of *nyamplung* oil, methanol and BMIMHSO<sub>4</sub> as catalyst. Equipment used in study was batch reactor equipped with temperature sensor with microwave heating system. The research variables studied were reaction temperature (50-70°C), molar ratio oil to methanol (1:30-1:60) and catalyst concentration (5-17.5%). The result of esterification reaction was analyzed by FFA (free fatty acid) content using titration analysis. The best free fatty acid (FFA) result was 1.92%, with molar ratio of oil to methanol was 1:40, catalyst concentration was 15% by weight and at 60°C for 120 min. The esterification of *nyamplung* oil meets the criteria as biodiesel feedstock.

*\*This is a revised and extended version of an article which had been presented at SNTK UNNES 2017, Semarang, Indonesia, September 20<sup>th</sup>, 2017.*

## INTRODUCTION

World petroleum availability continues to dwindle as demand for petroleum energy increases. Diesel oil from petroleum demand continues to increase so it needs to be overcome with renewable fuels ie biodiesel (Said et al., 2010).

Biodiesel production from nyamplung (*Calophyllum inophyllum*) oil is a potential non edible oil in Indonesia. The productivity of nyamplung oil in Indonesia is high at 20 ton / ha (Bustomi et al., 2008). Oil content from nyamplung seeds is high by 40-73% (Soerawidjaja, 2006). Nyamplung seed oil is a source of renewable energy without competing with food needs. Nyamplung oil with high FFA content of 21.62%, can not be

directly done for transesterification process and have to do esterification process first to decrease FFA level.

The selection of energy sources for the biodiesel manufacturing process is very important considering that biodiesel is a new energy source that emphasizes the effectiveness of energy use. The use of microwave energy in biodiesel production processes can decrease the time required for the reaction when compared with conventional methods (Matoseni & Ani, 2012).

In the process of making biodiesel the role of catalyst is very important, the use of acid or base catalyst has a weakness that is not environmentally friendly. Ionic liquid is used as an environmentally friendly catalyst and for the synthesis of biodiesel

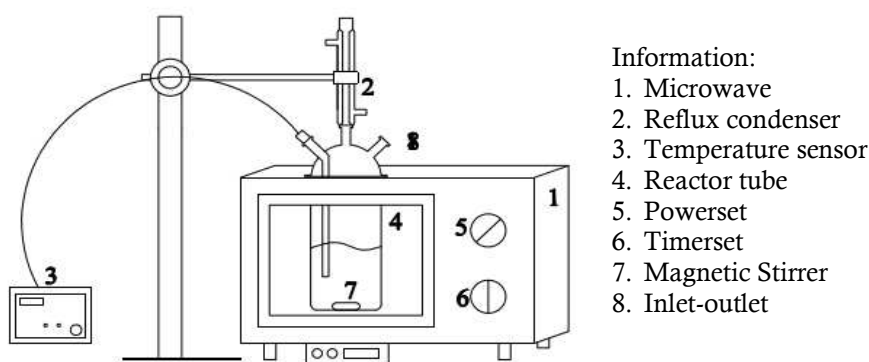


Figure 1. Scheme of Esterification Instrument

due to its favorable characteristics such as high catalytic activity, high selectivity, and available for recycling.

The study of Muhammad et al. (2014), esterification on the manufacture of biodiesel with nyamplung oil-based using microwave requires 60 minutes esterification time, operating conditions at 100W microwave power, with sulphate acid catalyst and continued transesterification process takes 60 minutes with CaO solid catalyst, resulting biodiesel yield of 94%. Research Lieu et al. (2013) The esterification process using micro-oil wave Cieba petandra takes 12 minutes and operating temperature 60°C, sulfuric acid catalyst yields FFA conversion 94.43% (Lieu et al., 2013). The study of Li et al. (2014), ionic liquid type 1-Butyl-3-methylimidazolium hydrogen sulfate (BMIMHSO<sub>4</sub>) catalyst can be used as a biodiesel production process in an esterification reaction of oleic acid by conventional process at a temperature of 130 °C takes 4 hours and produces a yield ester amounted to 97.7%. The study of Fauzi et al (2013), biodiesel production using ionic liquid catalyst BMIMHSO<sub>4</sub> in esterification reaction biodiesel process from oleic acid with conventional process at temperature 87°C takes time 5.4 hour and the yield was 81.2%.

The study of esterification reactions on biodiesel production using 1-butyl-3-methylimidazolium hydrogen sulphate and microwave-assisted catalysts is not yet available in published literature. Therefore, in this study learned the factors that influence the esterification reaction of biodiesel synthesis with ionic liquid catalyst 1-butyl-3-methylimidazolium hydrogen sulphate and microwave-assisted in *nyamplung* oil.

## METHOD

### Material

This study used nyamplung oil (*Callopyllum inopyllum*) containing free fatty acid (FFA) about 12.8% obtained from Kroya Cilacap Indonesia. Phosphoric acid concentration 85wt % in H<sub>2</sub>O purchased from Sigma Aldrich. The alcohol used in this study was methanol and the catalyst was ionic liquid 1 butyl-3 methyl imidazolium hydrogensulphate (BMIMHSO<sub>4</sub>). Methanol 99.9% purchased from Merck by PT. Hepilab Sukses Bersama Supplier Indonesia. Ionic liquid BMIMHSO<sub>4</sub> with a purity of 95.0% purchased from Sigma-Aldrich via PT. Hepilab Sukses Bersama Supplier Indonesia.

### Instrument

Scheme of research instrument on esterification process of biodiesel with microwave-assisted is presented in Figure 1.

### Work steps of Instrument:

The raw materials enter through the inlet on the reactor tube, then set the desired temperature. The stirrer and microwave are ignited, once the desired temperature is reached the catalyst is introduced into the reactor. The esterification process is carried out over a period of time.

### Pre-Treatment (Degumming) Stage

This stage aimed to eliminate the gum which consists of impurities, phospholida and protein. This process began by heating the nyamplung oil at 70°C and then added 0.3% phosphoric acid (w/w) nyamplung oil with stirring

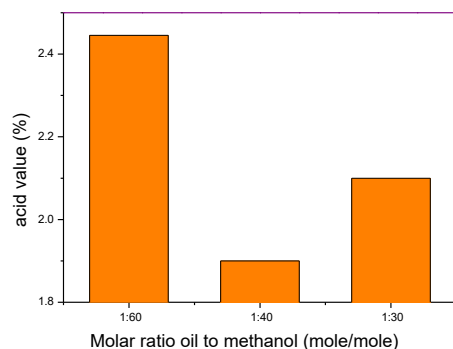


Figure 2. Effect of molar ratio of oil/methanol to acidity of nyamplung oil

for 25 minutes. Then washed using warm aquades (40°C) and separation in the separation funnel. The top layer (oil) was then heated to moisten the moisture content in the oil.

### Esterification Stage

The esterification reaction was carried out in a batch reactor using a three-neck tube and a condenser refrigerator with a microwave heater. Incorporate oil and methanol with a mole ratio of 1:40 oil/methanol to a three-necked tube. Adding ionic liquid catalyst with catalyst concentration variables 5%, 10%, 15%, 17.5% weight oil. Stirring with a magnetic stirrer and maintaining a constant temperature with variables 50°C, 55°C, 60°C, 65°C, and 70°C for variable time 20, 40, 60, 80, 100, 120, 140 minutes. After the reaction stopped, the mixture was inserted into the separating funnel to separate the methyl ester and then analyzed the acid number using titration method.

### Esterification Product Analysis

The analysis was done by titration method and then done by American Oil Chemist Society method (AOCS Official Methode Ca 5a-40,1998). Calculation of percent acidity is shown in Eq. 1.

$$\text{Acidity} = \frac{\text{mL KOH} \times \text{BMoxalic} \times \text{N KOH}}{\text{Sample Mass} \times 10} \times 100\% \quad (1)$$

## RESULTS AND DISCUSSION

### Effect of Oil-Methanol Molar Ratio

In determining the optimal operating conditions to obtain nyamplung oil with levels of FFA <2% to note some things, including the mole ratio of oil-methanol, catalyst concentration, temperature and time. The esterification reaction

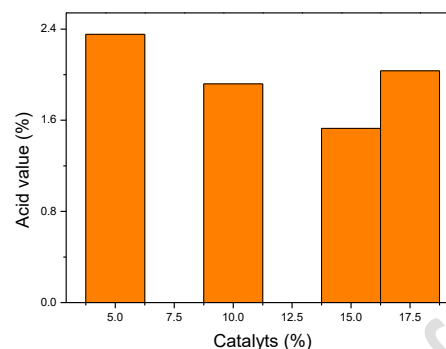


Figure 3. Effect of catalyst concentration on acidity value of nyamplung oil

takes place in a reversible manner, the reaction can be shifted to the right by giving excess methanol. In other words, there is an optimum volume of methanol resulting in the best product conversion (Usman et al., 2009).

The effect of oil/methanol molar ratio variation was studied at 1:60, 1:40, and 1:30, with operating conditions at 60 °C, catalyst 10% by weight to oil and reaction time 120 minutes. The esterification reaction was carried out by the amount of excess methanol which aimed to shift the equilibrium of the esterification reaction so that the equilibrium shifts toward the product. The results of experiments were presented in Figure 2, the percentage of acidity of 2.44%, 1.92% and 2.1% for the molar ratio of oil/methanol 1:60, 1:40, and 1:30, respectively. The best result was obtained in molar ratio of oil/methanol 1:40 with acidity value 1.92%. The study of Muhammad et al. (2014), conveyed that the best reaction conditions in the mole ratio of 1:40 oil-methanol with the concentration of 13% H<sub>2</sub>SO<sub>4</sub> (v/v) catalyst with the final FFA level of 1.13%.

### Effect of Catalyst Amount

For studying the effect of catalyst concentration, the research was conducted on the catalyst concentration range 5-17.5% to oil weight, with fixed ratio of 1:40 oil/methanol ratio (best ratio), temperature 60°C and reaction time 120 minutes. The experimental results of the effect of the amount of catalyst on the percent acidity were presented in Figure 3, the percentage of acidity respectively 2.35%, 1.92%, 1.52% and 1.52% for the catalyst amount of 5%, 10%, 15% and 17.5%. The best results were obtained on the amount of catalyst 15% by weight to the weight of the oil. In Figure 3 showed that at a concentration of ionic liquid

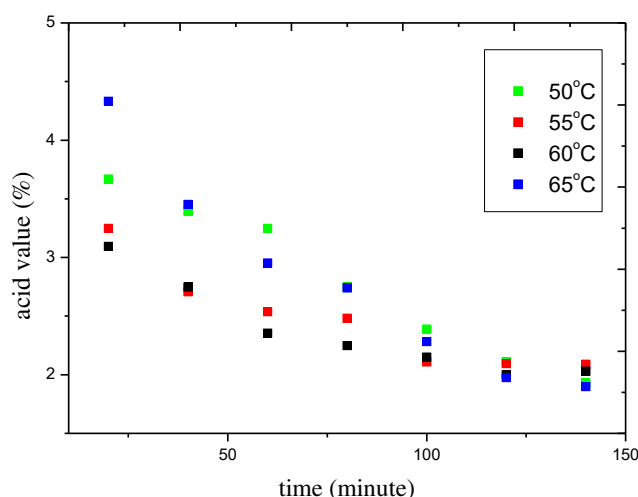


Figure 4. Influence of reaction time to acidity of oil nyamplung on temperature variation

catalyst BMIMHSO<sub>4</sub> is 5 wt% resulting in a percentage of acidity 2.35. When the catalyst concentration was increased, the resulting acidity value was smaller, this was due to the presence of a catalyst which could decrease the activation energy. In the concentration of ionic liquid catalyst is 15% is the best condition that yields acidity value of 1.52%. At 17.5% catalyst concentration gives darker product yield and slower acidity value. As mentioned Ramadhas et al. (2005) the excess of the acid catalyst will cause a dark color solution and a decrease in the acidity value slowly in the esterification process.

#### Effect of Temperature and Time

In addition to the mole ratio, catalyst percentage, operating time and temperature also affect the final acidity value of esterification reaction results. To study the effect of temperature and time is done with the ratio of 1:40 ratio (best ratio) with the concentration of liquid ionic catalyst BMIMHSO<sub>4</sub> 15% (% weight of the best catalyst). The effect of time on acidity values on temperature variations was shown in Figure 4. Figure 4 showed that there was a decrease in acidity values from 20 minutes to 120 minutes, while from 120 to 140 minutes the acidity tends to be constant, increasing the reaction temperature can result in the number of collisions effective to produce methyl esters. The best result was achieved at esterification reaction temperature 60°C with acidity value 1.92%.

#### CONCLUSION

The esterification reaction of nyamplung oil (*Calophyllum inophyllum*) with ionic liquid

catalyst 1 butyl-3-methylimidazolium hydrogen sulphate (BMIMHSO<sub>4</sub>) assisted with microwaves, the best result was achieved with the acidity of 1.92%. The esterification reaction conditions were achieved at an oil/methanol molar ratio of 1:40 mol/mol, a catalyst concentration of 15% by weight to oil, a temperature of 60 °C and for 120 minutes. Nyamplung oil esterification reaction results meet the criteria as raw materials of biodiesel.

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