# Artikel 2

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# Process Evaluation of Biodiesel Production from *Nyamplung* (*Calophyllum inophyllum*) Oil Enhanced by Ionic Liquid + NaOH Catalyst and Microwave Heating System

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**ABSTRACT:** *Biodiesel production using conventional method usually involves a long processing time and produces low yield. In Indonesia, nyamplung (Calophyllum inophyllum) plant is a highly potential raw material for biodiesel production with plantation areas of approximately 255.350 ha and produces about 20 tonne ha$^{-1}$ seeds per year. The oil in the seed is about 50%–73%, and mainly consists of oleic and linoleic acid. The crude nyamplung oil has a free fatty acid of approximately 12.9%. Based on literature, the microwave has been intensively applied to reduce the processing time while ionic liquid has also been used as an acceleration agent in the transesterification reaction during biodiesel production. In the present study, biodiesel was produced from nyamplung oil using an ionic liquid (BMIMHSO$_4$) + NaOH as a catalyst and assisted by microwave heating system. The effect of transesterification reaction temperature (i.e., range of 50°C–80°C); molar ratio of methanol to oil (range of 6–12 mole/mole); reaction time (range of 3–9 min); and microwave power (range of 100–400 W) were studied. Catalyst concentration was fixed at BMIMHSO$_4$(1):NaOH(1), i.e., 1%. Based on the results, the optimum condition was achieved at 70°C with yield of 94.04%, molar ratio of methanol to oil 9 mole/mole and reaction time 6 min, and microwave power at 200 W with yield of 93.83%.*

**Keywords:** Biodiesel, *nyamplung*, transesterification, microwave, *Calophyllum inophyllum*

## 1. INTRODUCTION

Biodiesel is a potential alternative fuel to fossil fuels. Biodiesel can be produced from vegetable oil or animal fat through transesterification reactions. *Nyamplung* (*Calophyllum inophyllum*) seed oil is abundant in Indonesia and its potential has not been fully utilised. *Nyamplung* seed has a high oil content of about 75%, mainly consisting of oleic acid and linoleic acid, which is about 71%.[1] Crude *nyamplung* oil has a high acid content of 12.9% and also contains gum. Therefore, it requires a pretreatment process before being used as a raw material for biodiesel. The pretreatment process of crude *nyamplung* oil combines degumming and neutralisation processes. Biodiesel is produced by transesterification reaction between oil and alcohol. Some parameters may affect the transesterification reaction, such as temperature, catalyst concentration, molar ratio of methanol to oil, and reaction time.[2]

Microwave heating is more effective than conventional heating. This heating can increase the chemical reaction because it can transfer energy directly to the reactant so that heat transfer and reaction could be faster.[3] Heating systems with microwave radiation can be used in biodiesel production.[4,5] In renewable energy production, yield and selectivity can be improved by using microwave technology.[6] Microwaves absorb polar compound well and methanol is a polar compound, thus it is very compatible in the production of biodiesel by using microwaves.[7] The microwave heater may cause increase in the polar solvent boiling point compared with conventional heating.[8]

Li et al. found that microwave-assisted biodiesel production from *Camptotheca acuminata* seed oil, catalysed by [$BSO_3HMIM]HSO_4$-$Fe_2(SO_4)_3$ 5wt% at 60°C for 60 min gave the highest yield of 95.7%. Zhou et al. studied transesterification of glycerol trioleate with catalyst 1-butyl-3 methyl imidazolium hydroxide, reaction temperature 120°C, molar ratio MeOH to oil 9, and reaction time of 8 h has obtained a yield of 87.2%.[9,10] Liang et al. studied the synthesis of biodiesel from soybean with catalyst [Et3NH] Cl-$AlCl_3$ (x $AlCl_3$ = 0.7), and reaction temperature 70°C using conventional heating for 9 h. They obtained biodiesel yield of 98.5%.[11]

The transesterification reaction during the biodiesel production is considered a slow reaction, therefore a catalyst is needed to increase the reaction rate by decreasing the activation energy of reaction. In the transesterification reaction, the use of alkaline catalyst at a low temperature is proven to give a faster reaction time than acid and enzyme catalysts. However, alkaline catalysts have deficiencies as it has a tendency to cause saponification, which is due to the free fatty acid content in the oil.[12] The use of homogeneous catalyst still produces biodiesel with low yield.

Therefore, to increase the yield of biodiesel, the use of ionic liquid as a catalyst is highly considered. Research on the production of biodiesel using ionic liquid as a catalyst and microwave as a heating system has been studied.

Ionic liquid is a potential catalyst to be used in biodiesel production.[13,14] It is a new generation of environmentally friendly chemicals with high catalytic activity.[15] Ionic liquid is a kind of organic salt composed of anions and cations in a liquid state at temperatures below 100°C and its vapour pressure characteristic is negligible.[16,17] Sherbiny et al. showed that the synthesis of biodiesel from jatropha oil produced the highest yield of 94.7% with 2 min reaction time using microwave heating while conventional heating requires 1 h reaction time.[5] To the best of our knowledge, the study of biodiesel production using a mixture of an ionic liquid, i.e., 1-butyl-3 methyl imidazolium hydrogen sulfate ($BMIMHSO_4$) with NaOH as a catalyst is not yet available in the published literature. In the present study, the effects of using a mixture of $BMIMHSO_4$+ NaOH with several parameters, i.e., reaction temperatures and microwave powers by using microwave radiation on the transesterification of *nyamplung* oil has been investigated.

## 2. EXPERIMENTAL

### 2.1 Materials

The main raw material used in this study is *nyamplung* oil containing free fatty acid (FFA) about 12.8%, which was obtained from Kroya Cilacap, Indonesia, whereas, 99.9% methanol and 99.0% NaOH were purchased from Merck. The ionic liquid $BMIMHSO_4$ with purity of 95.0% was purchased from Sigma-Aldrich.

### 2.2 Pretreatment of Crude *Nyamplung* Oil

Crude *nyamplung* oil containing gums was removed via degumming method. About 20% phosphoric acid 0.3% (v/wt) was added to *nyamplung* oil and then heated to 70°C for 25 min.[18] Reduction of *nyamplung* oil free fatty acid was carried out by neutralisation process, by adding saturated sodium carbonate solution (20 ml per 100 ml) into the mixture and heated at 70°C for 1 h. Soap and gum are separated from the oil by decantation for 24 h. The oil from the decantation was washed with water at 60°C–70°C to obtain a neutral pH of oil and then heated at 80°C to evaporate water.

## 2.3 Transesterification Assisted by Microwave Heating System

The transesterification reaction was carried out in a batch reactor equipped with microwaves, condensers, temperature sensors and magnetic stirrers. Stirring speed was kept constant at 600 rpm. The oil was placed in the reactor and heated first to the desired temperature. The amount of catalyst $BMIMHSO_4 + NaOH$ in the ratio of 1:1 was added to the reactor about 1% by weight of the oil. The molar ratio of methanol to oil was in the range of 6 to 12 mol/mol and reaction time was in the range of 3–9 min. The reaction temperature was varied from 60°C to 80°C and power microwave at 100–400 W. The product was added to the separator until two phases were formed in equilibrium. The upper phase consists of methyl esters, and the lower phase contains glycerol. Upper phase samples were taken and analysed using a gas chromatography-mass spectrometry (GC-MS) to determine the concentration of methyl esters. The results of methyl esters were defined as follows:[12]

Methyl ester yield = methyl ester concentration × biodiesel yield:

$$= Cx\frac{W_b}{W_{oil}}x100\% \qquad (1)$$

where $C$ is methyl ester content (%), $W_b$ is the weight of biodiesel production (g), and $W_{oil}$ is the weight of initial amount of *nyamplung* oil (g).

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR Analysis

The Fourier transform infrared (FTIR) spectrum of the biodiesel produced from *nyamplung* oil with $BMIMHSO_4$-NaOH 1% catalyst condition, 6 min reaction time and molar ratio methanol to oil 1:9 is presented in Figure 1.

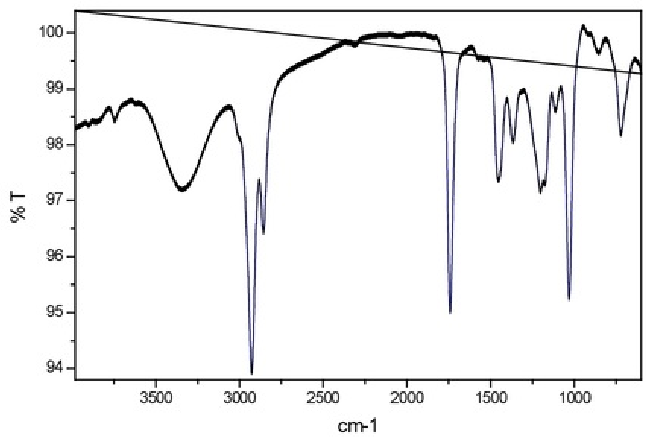


Figure 1: Spectrum FTIR for a FAME sample of *nyamplung* oil.

In the 1750–1730 $cm^{-1}$ region, it can be observed that its peak can be attributed to the C=O stretch, a typical ester found in biodiesel and triglyceride spectra.[19] The main spectral region of biodiesel is in the range of 1450–1375 $cm^{-1}$. The peak at 1452 $cm^{-1}$ corresponds to the asymmetric stretching $-CH_3$ in the biodiesel spectrum. The 1366 $cm^{-1}$ peak can be attributed to the glycerol group $O\text{-}CH_2$ (mono-, di- and triglycerides), present in the triglyceride spectrum. Stretching $O\text{-}CH_3$ is shown by absorbance at 1201 $cm^{-1}$ which is a biodiesel.

### 3.2 Effect of Transesterification Temperature

The experiments were carried out with the catalyst $BMIMHSO_4$(1): NaOH(1) 1%, reaction time 6 min, molar ratio of methanol to oil 9 and various reaction temperature (50°C, 60°C, 70°C and 80°C) to investigate the influence of temperature on the biodiesel yield. As shown in Figure 2, the yields are 86.84%, 92.81%, 94.04% and 84.08% for 50°C, 60°C, 70°C and 80°C, respectively. The results showed that increase in temperature from 50°C to 70°C significantly increased the biodiesel yield from 86.84% to 94.04%. When the temperature was further increased to 80°C, the yield decreased to 84.08%.

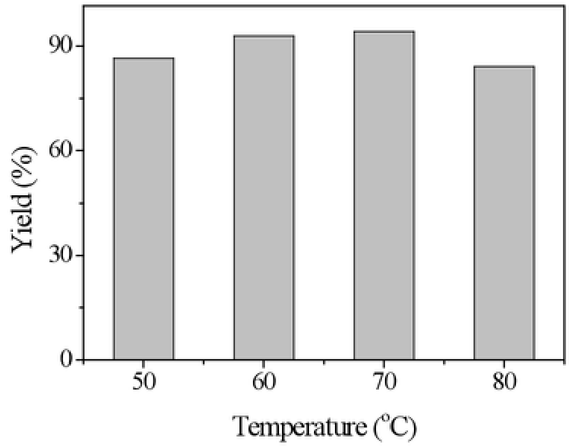

Figure 2: Effect of reaction temperature on yield with microwave heating.

The results obtained can be explained as follows. The biodiesel yield is influenced by temperature, in which a high reaction temperature will decrease the viscosity of the oil so that it will increase the reaction rate and shorten the reaction time.[20] The solubility of the oil in methanol will increase with the high reaction temperature, thus improving the conversion of biodiesel. However, high temperatures also cause saponification that lower the yield.[21]

### 3.3 Effect of Molar Ratio Methanol to Oil

Stoichiometrically, the transesterification reaction requires 3 moles of methanol for 1 mole of triglyceride, which produces 3 moles of fatty acid alkyl ester and 1 mole of glycerol. The transesterification is a reversible reaction, hence a large excess of methanol is required to push the reaction to the right direction.[20]

The experiments were carried out with catalyst $BMIMHSO_4$(1):NaOH(1) amount of 1.0 wt% of oil, reaction time of 6 min, reaction temperature 70°C and various molar ratios of methanol 6, 9 and 12 mole/mole. The effect of molar ratio of methanol to oil on the yield of biodiesel is shown in Figure 3.

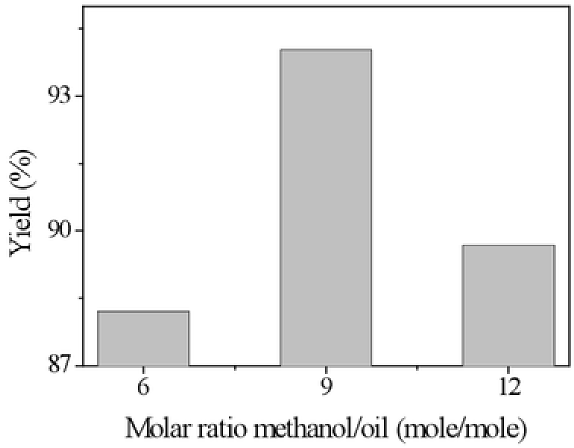


Figure 3: Effect of molar ratio of methanol to oil on yield with microwave heating.

As shown in the figure, increasing molar ratio of methanol to oil from 6 to 9 mole/mole increased the yield from 88.21% to 94.04%. When the molar ratio was further increased to 12 mole/mole, the yield decreased from 94.04% to 89.68%. The high molar ratio of methanol to oil increased the solubility of glycerol, thus the glycerol will be difficult to separate and went into the biodiesel phase, which then decreased the yield of biodiesel.[2]

### 3.4 Effect of Reaction Time

The experiments were carried out with catalyst $BMIMHSO_4$(1):NaOH(1) amount of 1.0 wt%, reaction temperature 70°C and molar ratio of methanol to oil of 9 mole/mole. The reaction time was varied at 3 min, 6 min and 9 min in order to investigate the influence of reaction time on the yield of biodiesel. As shown in Figure 4, the yields are 89.81%, 94.04% and 93.39% for reaction time of 3 min, 6 min and 9 min, respectively. The results showed that increase in reaction time from 3 min to 6 min increased the yield from 89.81% to 94.04%. When the reaction time was increased to 9 min, the yield did not change significantly (i.e., 94.04% to 93.94%). Therefore, the optimum reaction time that gave the best yield was 6 min.

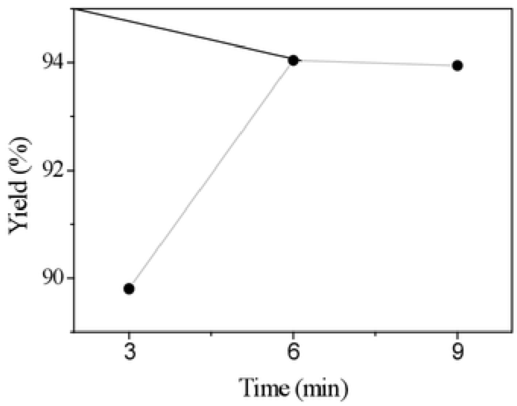


Figure 4: Effect of time reaction on the yield.

This result was similar with other research studies. Leung et al. found that maximum yields were achieved at reaction times of less than 90 min, and further increase in reaction time did not increase the biodiesel yield.[20] Leung et al. also stated that excessive reaction time will cause the transesterification reaction run to the left so that it will decrease the product yield, due to the loss of esters and many fatty acids converted into soap.

### 3.5 Effect of Microwave Power

To study the effect of microwave power on biodiesel yield, the experiments were carried out at various microwave power, i.e., 100 W, 200 W and 400 W. Whereas, other parameters were fixed, i.e., $BMIMHSO_4$ (1):NaOH (1) amount 1.0 wt%, reaction time 6 min, the molar ratio of methanol to oil 9. The results of experiments are presented in Table 1. As seen in the table, the yield of biodiesel were 92.08%, 93.8% and 92.27% for 100 W, 200 W and 400 W, respectively. The results showed that the increase of microwave power from 100 W to 200 W significantly increased the yield from 92.08% to 93.8%. When the microwave power was increased further to 400 W, the yield decreased from 93.8% to 92.27%.

Table 1: Effect of microwave power.

| Microwave power | Yield (%) |
|---|---|
| 100 | 92.08 |
| 200 | 93.80 |
| 400 | 92.27 |

The effect of microwave power on the transesterification reaction has been reported by other researchers. Khemthong et al. reported that transesterification reaction using CaO catalyst 15 wt%, microwave power operation condition 900 W, methanol to oil ratio 18 and reaction time of 4 min produced maximum biodiesel yield of 96.7%.[22] Microwave energy increased intensity of localised heating and accelerated the chemical reactions, resulting in high yield of biodiesel (in a short time).[5,23] Handayani et al. also reported that the transesterification using microwave required shorter reaction times than conventional heater.[24] Additionally, microwave heating gave a yield of 92.81% with reaction time of 6 min, while conventional heating took 180 min to reach similar yield, i.e., 93.89%. This phenomenon could be explained in the following. The methanol has a high microwave absorption capacity and it is an organic solvent with high polarity, a property that supports the rapid transesterification reaction caused by polarisation of dipolar and ionic conduction.[25] The boiling point of polar solvents increase when heated by using microwave over conventional heating, which is called superheating. The more polar the solvent, the effect of microwave will be accelerated with increasing temperature.[8]

## 4. CONCLUSION

Biodiesel from *nyamplung* oil has been successfully produced via transesterification reaction. The reaction used catalyst $BMIMHSO_4$ + NaOH in the ratio of 1:1 (1 wt% of oil) and assisted by microwave heating system. The effect of transesterification reaction temperature (i.e., range of 50°C–80°C); molar ratio of methanol to oil (i.e., range of 6–12 mole/mole); reaction time (i.e., range of 3–9 min); and microwave power (i.e., range of 100–400 W) were studied. The best results were obtained at reaction temperature of 70°C, molar ratio of methanol to oil 9 mole/mole and reaction time 6 min with yield of 94.04%, and microwave power of 200 W with a yield of 93.83%.

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