Artikel 10

by Prima Astuti

Submission date: 02-Dec-2019 08:38AM (UTC+0700) Submission ID: 1224635306 File name: PPCE_2019.pdf (1.46M) Word count: 5460 Character count: 27550 Periodica Polytechnica Chemical Engineering, 63(3), pp. 406–413, 2019

Response Surface Optimization of Biodiesel Production from Nyamplung (*Calophyllum inophyllum*) Oil Enhanced by Microwave and Ionic liquid + NaOH Catalyst

Prima A. Handayani^{1,2*}, Abdullah Abdullah², Hadiyanto Hadiyanto²

* Corresponding author, e-mail: prima@mail.unnes.ac.id

Received: 08 August 2018, Accepted: 05 November 2018, Published online: 30 January 2019

Abstract

Nyamplung (*Calophyllum* inophyllum) plant is a highly potential raw material in the biodiesel production, the oil in the seeds is 50-73 %. The microwave has been intensively applied to reduce the processing time while ionic liquid also was used as an acceleration agent in the biodiesel production. The optimum process condition of the biodiesel production using lonic liquid + NaOH as a catalyst mixture and assisted with microwave heating system were determined in this study. Response Surface methodology (RSM) was used to optimize three transesterification maction variables: the catalyst concentration of (0.5-1.5 %wt), the reaction temperature of 60-80 °C, and methanol to oil molar ratio of 6:1-12:1, while the transesterification time was set constant at 6 minutes. The optimization showed that the maximum biodiesel yield can be obtained was 95.8 % at the catalyst concentration of 1.2 %wt, the reaction temperature of 71.3 °C, and methanol to oil molar ratio of 10.8 mole/mole.

Keywords

biodiesel, transesterification, ionic liquid, microwave

1 Introduction

Biodiesel production has attracted numerous attentions due to its potential to substitute and to minimize the severe issues of fossil fuel. Biodiesel is a biofuel which can be produced from esterification of vegetable oil or animal fats. Nyamplung (Calophyllum inophyllum) is a plant which commonly found in Indonesia and its seed contains 75 % oil, including an unsaturated fatty acid of 71 % [1]. Crude Nyamplung oil also contains gums and free fatty acids up to 12.9 %. The pretreatment processes of crude oil such as degumming and neutralization are normally needed before processed to biodiesel. Oils or fats are reacted with alcohol (transesterification reaction) to produce fatty acid alkyl esters (biodiesel). The parameters affecting the transesterification reaction are temperature, catalyst concentration and molar ratio of methanol to oil [2]. The production of biodiesel from oil uses acid, base or biological catalysts to enhance the reaction. The base catalyst can take place at a low temperature and the reaction time relatively faster than acid and biological catalyst. However the base

catalyst has a drawback such as it can cause the saponification due to high content of free fatty acid in the oil [3]. In addition, the use of homogeneous catalyst still produces low biodiesel yield and require a longer processing time. Therefore, another approach is required to reduce the time and increase the yield. One method is by using ionic liquids as catalyst and external power to accelerate the reaction.

The study of the biodiesel production using ionic liquids as a catalyst and microwave as a heating system were recently studied. The use of ionic liquids has been a widely studied in the recent years because it has the potential as a catalyst in the biodiesel production [4]. The ionic liquid catalyst is a new generation of environmentally friendly chemical with a high catalytic activity as the advantages property [5]. The ionic liquid is a kind of organic salt composed of anions and cations in a liquid state at a temperature below 100 °C [6]. The ionic liquid characteristics have many advantages such as negligible vapor pressure and have good solubility for organic and inorganic materials [7].

Cite this article as: Handayani, P. A., Abdullah, A., Hadiyanto, H. "Response Surface Optimization of Biodiesel Production from Nyamplung (*Calophyllum inophyllum*) Oil Enhanced by Microwave and Ionic liquid + NaOH Catalyst", Periodica Polytechnica Chemical Engineering, 63(3), pp. 406-413, 2019. https://doi.org/10.3311/PPch.12965

¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Gedung E1 Lantai 2 Fakultas Teknik, Kampus UNNES Sekaran Gunungpati, Semarang 50229, Indonesia

² Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Jl. Prof. Soedarto S.H., Tembalang, Semarang 50239, Indonesia

Microwave radiation can be used as a promising heating system in the biodiesel production [8, 9]. Microwave heating can enhance chemical reactions because it can transfer energy directly to the reactants such that the heat transfer is more effective than conventional heating and the reaction can take place more quickly [10]. Polar molecules interact to absorb microwave, and non-polar molecules will be inert. It can be analyzed that the polar solvents can lead to increase boiling point when heated by using microwave heating than conventional heating [11].

El Sherbiny et al. [9] showed that the synthesis of biodiesel from jatropha oil produce the highest yield of 94.7 % with a reaction time of 2 minutes using microwave heating while conventional heating requires a reaction time of 1 hour. As our best knowledge, the optimization study of the biodiesel production using the mixture of the 1 butyl-3 methyl imidazolium hydrogen sulphate ionic liquid with NaOH as a catalyst still not available in the published literature. Therefore, in the present study, the effect of the use of ionic liquid + NaOH catalyst and microwave radiation on transesterification of Nyamplung oil were investigated and optimized using Response Surface Methodology (RSM). This optimization method was used, since it is very suitable for the exploration of complex processes [12]. RSM with a central composite design was used to optimize the transesterification of Nyamplung oil with respect to the catalyst concentration, the temperature and the molar ratio methanol to oil.

2 Materials and Methods

2.1 Materials

The ionic liquid of 1 butyl-3 methyl imidazolium hydrogensulfate (BMIMHSO₄) with the purity of 95.0 % purchased from Sigma- Aldrich through PT. Hepilab Sukses Bersama supplier, Indonesia. Methanol and sodium hydroxide have the purity of 99.9 % and 99.0 %, respectively and supplied by Merck through PT. Hepilab Sukses Bersama supplier, Indonesia. Phosphoric acid with the purity of 85.0 % was supplied by Sigma-Aldrich and technical grade sodium carbonate was obtained from PT. Hepilab Sukses Bersama supplier. Nyamplung crude oil contains 12.9 % of FFA and viscosity of 63.03 mm²/s was obtained from Kroya, Cilacap, Indonesia.

2.2 Methods

2.2.1 Pretreatment

Crude Nyamplung oil contains gums and free fatty acid (FFA) of 12.9 %, it was purified using degumming and neutralization method to remove the impurities present in the oil. Phosphoric acid with the concentration of 20 % was prepared, it was then added into the oil with amount of 0.3 % (v/wt). The mixture was then heated on a hot plate at 70 °C for 25 minutes. Furthermore, saturated solution of sodium carbonate with a concentration of 20 ml / 100ml oil was added into the oil. It was then heated at 70 °C for 1 hour. 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. Pure Nyamplung oil has free fatty acid of 0.21 %.

2.2.2 Transesterification assisted by Microwave power

Transesterification reaction was conducted in a fournecked batch reactor with a volume of 500 mL equipped with microwave, condenser, temperature sensor and magnetic stirrer set at 600 rpm. A fined amount of Nyamplung oil was placed into the reactor, which was preheated to the desired temperatures in a microwave before starting the reaction. The amount of [BMIMHSO₄] and NaOH catalyst at a ratio of 1:1 was varied at a range of 0.5-1.5 %wt to the oil. The molar ratio of methanol to oil was varied from 6 to 12 mole/mole and the reaction temperature from 60 to 80 °C. The reaction time of microwave heating was fixed at 6 minutes. The reaction mixture was added into the flags separator until two phases are formed in equilibrium. The upper phase consisted of methyl esters, and the lower phase contained the glycerol.

The methyl ester phase was injected into Gas Chromatography-Mass Spectrometry (GC-MS) (QP2010S SHIMADZU) with a syringe to determine the concentration of methyl ester (oleic acid, linoleic acid, stearic acid and palmitic acid). The column used was restek (RTX-1, 100 % dimethylpolysiloxane) 30 m \times 0.25 mm \times 0.25 µm). Within the GC-MS, the samples were analyzed with an oven temperature of 65 °C (8 minutes) and raised 10 °C min⁻¹ up to a temperature of 250 °C and held for 20 minutes. The methyl ester yield is calculated using Eq. (1) [3]

Methyl ester yield =
$$C \times W_b / W_{oil} \times 100 \%$$
. (1)

Where is methyl ester content (%), represents weight of biodiesel production (g) and W_{oll} is the weight of initial amount of Nyamplung oil (g).

2.3 Response surface methodology design

RSM with a Central Composite Design (CCD) was employed to design the experiment and investigate the influence of the three independent variables. The independent variables were catalyst concentration, reaction temperature and methanol to oil molar ratio. Catalyst concentration 0.5, and 1.5 %wt, temperature reaction at 60, 70 and 80 °C and molar ratio methanol to oil of 6, 9 and 12 mole/mole. The methyl ester yield was selected as the responses for the combination of these independent variables. The real value of the independent variables was transformed to the coded variables, shown in Table 1.

The yield of methyl ester is expressed as a function of a set of independent variables, following a second order polynomial equation as shown in Eq. (2) [13]

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{\substack{i=1\\i < j}}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \varepsilon.$$
(2)

Where various x_i and x_j are independent variables, respectively, y is response variables; β_0 , β_i , β_{ij} , β_{ij} are the regression coefficients and k is the number of variables.

In this investigation, the three independent variables were catalyst concentration (X_1) , temperature reaction (X_2) and molar ratio methanol to oil (X_3) and Y was response variable (methyl ester yield) yielding the Eq. (3)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2.$$
(3)

2.4 Statistical Analysis

The Statistica 6.0 software was used to analyze experimental data and calculate the value of the prediction response. The software can also generate graphs plot response values which are predicted in 3-D plot. The significance evaluation between the mean of methyl ester concentrations with different experimental runs were statistically defined at (p) < 0.05. The validity of developed model equation was verified by conducting an experimental study.

3 Results and Discussion

3.1 The development model for the methyl ester yield prediction

Model parameters in Eq. (3) were statistically determined by using response surface methodology (RSM) based on Central Composite Design (CCD). Table 2 shows the

Table 1	l Experimental	range and	factor le	vel of	process variable	•
---------	----------------	-----------	-----------	--------	------------------	---

Indonen deut Verichle	Pattern Code					
Independent Variable	-α	-1	0	+1	$+\alpha$	
Catalyst, %wt	0.2	0.5	1.0	1.5	1.8	
Temp, °C	53.2	60.0	70.0	80.0	86.8	
MeOH:TG, (mole/mole)	4.0	6.0	9.0	12.0	14.1	

experimental design with three factors which are methanol to oil molar ratio, reaction temperature and catalyst concentration. The prediction model was validated with the experimental data to suggest that the appropriate predictive models to estimate the experimental data. Therefore, the model and the experimental data should have a high coefficient of correlation (R^2). The analysis of variance (ANOVA) of experimental data is shown in Table 3. It shows that the R^2 value of the model is 0.97014 indicating that 97.014 % of the experimental data can fit to the predicted value of the methyl ester yield model (Fig. 1).

In addition, the *p*-value of the model parameters indicates that the developed model predictions parameters were significant [14]. The *p*-value mostly below 0.05, except for β_{12} in yield model (p = 0.06029), β_{13} in the yield model (p = 0.615856) and β_{23} in the yield model (p = 0.805990). The results of the analysis stated a mathematical model for the methyl esters yield prediction with a very well fit to the second order polynomial formula as defined in Eq. (4) by neglecting insignificant variables which are β_{12} , β_{13} and β_{33}

$$Y_{methyl\ ester} = -63.8588 + 19.4043X_1 + 3.4187X_2 +4.9059X_3 - 14.8547X_1^2 - 0.0257X_2^2 - 0.2461X_3^2.$$
(4)

Table 2 The set of experimental variables based on Central Composite Design and observed response of methyl ester yield in the synthesis of biodiesel with catalyst IL + NaOH and assisted microwave.

Run	Catalyst (%wt)	Temp	Temp MeOH:TG, (°C) mole/mole	Experimental Value	Predicted Value
	(/000)	(0)	more more	Yield (%)	Yield (%)
1	0.5	60.0	06.0	81.37	82.50
2	0.5	60.0	12.0	87.49	87.10
3	0.5	80.0	06.0	82.40	81.12
4	0.5	80.0	12.0	85.83	86.16
5	1.5	60.0	06.0	83.91	84.13
6	1.5	60.0	12.0	87.81	89.63
7	1.5	80.0	06.0	85.51	86.44
8	1.5	80.0	12.0	91.95	92.37
9	0.2	70.0	09.0	79.91	80.88
10	1.8	70.0	09.0	89.22	87.47
11	1.0	53.2	09.0	87.63	86.83
12	1.0	86.8	09.0	87.96	87.98
13	1.0	70.0	04.0	83.73	83.99
14	1.0	70.0	14.1	93.88	92.85
15C	1.0	70.0	09.0	94.04	94.68
16C	1.0	70.0	09.0	95.18	94.68
17C	1.0	70.0	09.0	94.63	94.68
18C	1.0	70.0	09.0	95.23	94.68
19C	1.0	70.0	09.0	94.20	94.68

98 96 Yield of Methyl Ester ideal line; x=y 94 % ---- 95% PI 92 Predicted Yield, 90 88 86 84 82 80 78 86 88 90 92 94 78 80 82 84 96 98 Experiment Yield, %

Fig. 1 The correlation between the predicted value and experimental value of biodiesel yield ($R^2 = 0.9701$) with 95 % of Prediction Interval (PI).

3.2 Effect of transesterification parameters to methyl ester yield

the effect of parameters to the methyl ester yield is the catalyst concentration, the temperature, and the molar tio methanol to oil were studied. This parameter affects the reaction rate and yield of methyl ester. Temperature, the ratio of molar alcohol to oil and catalyst concentration are the most important parameters for biodiesel production [15]. High temperatures will imprease the solubility of oil in methanol, thus increasing the reaction rate and yield of methyl ester [16].

The molar ratio of alcohol to oil is one of the most important variables affecting the yield of methyl ester. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglycerides to produce three noles of fatty cid alkyl esters and one mole of glycerol [17]. However, a high molar ratio of alcohol to vegetable oil interferes with the separation of glycerine because there is an increase in solubility. When glycerin stays in the solution, it causes the equilibrium to return to the left, decreasg the yield of methyl ester [18]. The catalyst concentration can affect the yield of methyl ester. Increased catalyst conentration will increase the conversion of triglycerides and increase the yield of methyl esters. the optimal value of catalyst concentration (NaOH) is 1.5 %wt and the addition of an excess alkali catalyst causes more triglycerides to react with alkaline catalysts and form more soap [17].

The results of the analysis in Fig. 2 shows that the catalyst concentration effect to the yield of methyl ester, with increasing concentration catalyst to higher yield. In Table 3, the parameter catalyst concentration has a value of p = 0.022637,



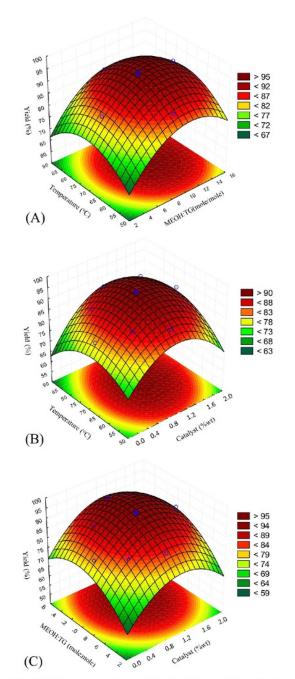


Fig. 2 The 3D response surfaces profile of methyl ester yield as affected by independent variable

catalyst concentration significantly affect to the methylester yield. At a constant temperature conditions of 70.5 °C and a molar ratio methanol to oil of 9.0 mole/mole, the methyl ester

Parameter	Predicted Coefficients	Standard Error	DF	p value
β_0	-63.8588	20.2103	1	0.0116
β_1	19.4043	7.0672	1	0.0226
β_2	3.4187	0.4858	1	0.0001
β_3	4.9059	1.2348	1	0.0032
β_{12}	0.1841	0.0857	1	0.0603 (<i>p</i> > 0.05)
β_{13}	0.1485	0.2857	1	0.6158 (<i>p</i> > 0.05)
β_{23}	0.0036	0.0143	1	0.8059 (p > 0.05)
β_{11}	-14.8547	1.3126	1	0.0000
β_{22}	-0.0257	0.0033	1	0.0000
β_{33}	-0.2461	0.0365	1	0.0001
Lack of fit			5	
R^2	0.9701		Adj R ²	0.9402
β_0	-63.8588		1	0.0116

Table 3 Prediction regression coefficients for second order polynomial models of method ester yield

yield increased from 84.5 % to 88.5 % across a concentration catalyst ranging between 0.16 and 1.0 %wt.

Table 3 also shows the *p*-value of 0.000061 for the temperature, significantly affect the methyl ester yield. Under a constant conditions of a concentration catalyst of 1.0 the methyl ester yield increased from 88.0 % to 89.0 %, across a temperature ranging between 50.0 and 70.5 °C.

In addition, for the molar ratio of methanol to oil with a value of p = 0.003239, significantly affect the yield of methyl ester. Under fixed conditions of the concentration catalyst of 1.0 %wt and temperature of 70.5 °C, the methyl ester yield increased from 82.5 % to 88.5 % across a molar ratio methanol to oil ranging between 2.0 and 9.0 mole/mole.

3.3 Optimization of operating conditions of transesterification reaction assisted by microwave power

A linear regression model to determine the optimum value of the concentration catalyst, reaction temperature and the methanol to oil molar ratio using RSM optimization is shown in Eq. (3). The results of this optimization analysis, the optimum value will be the catalyst concentration $(X_{1.opt})$, temperature $(X_{2.opt})$, and the molar ratio methanol to oil $(X_{3.opt})$. By using the optimal parameters, optimum yield is recalculated using Eq. (3).

Optimization results in Table 4 shows that the optimum conditions of microwave-assisted transesterification reaction of $X_{1,opt} = 0.298$, $X_{2,opt} = 0.1328$ and $X_{3,opt} = 0.61267$ represents the real condition of the catalyst concentration of

Table 4 The optimum value of yield methyl ester.						
Variables	Optimum condition (X_{op})		Value of response(Y_{opt})			
	Coded	Real value	Predicted	Experiment		
Catalyst, %wt	0.29	1.2				
Temperature, ℃	0.13	71.3	95.8 %	94.6 %		
MeOH:TG, (mole/mole)	0.61	10.8				
% error			1.26 %			
		_				

1.2 %wt, 71.3 °C temperature and index ratio of methanol to oil 10.8 mole/mole (Table 4). The results showed that the optimum yield was obtained in the range of studied variables as shown in Table 2. Optimum operation condition to produce methyl ester of 95.80 % was successfully predicted by the model. The result of the experiment (Table 4) showed that a methyl ester yield was 94.6% which are compared to the predicted value.

Microwave-assisted biodiesel production is shorter than conventional heating system. Handayani et al. [19] produced biodiesel from Nyamplung oil with catalyst [BMIMHSO₄] (1) + NaOH (1) amount of 1 %wt using conventional heating obtained yield (93.99 %) for 180 minutes, while using microwave assisted esterification method obtained the yield 92.81 % for 6 minutes. Lin et al. [3] indicated that the transesterification reaction with conventional heating systems using catalyst concentrations of NaNH, 1 %wt, reaction temperature of 65 °C, molar methanol-to-oil ratio of 8, and reaction time of 105 minutes, the yield was 95.6 % while with microwave for reaction time of 7 minutes obtained yield of 96.2 %. Methanol is a high polarity organic solvent and has a high absorption capacity of microwaves energy. Both of these properties are factors that support the rapid transesterification reaction caused by dipolar polarization and ionic conduction [20]. Polar solvents can make an increase in boiling point when heated using a microwave rather than conventional heating [11].

Microwave heating has several advantages over conventional heating such as reducing excess heat from the material surface, reducing thermal gradients, selective materials and volumetric heating, fast start-up and stop and reverse thermal effects [20]. While, conventional methods provide heterogeneous heating effects, depending on thermal conductivity, specific heat, and density of vessel materials. Vessel surface temperature is higher than the sample temperature in vessel. There are conventional energy sources are lost to the environment through material conduction and convection currents. Whereas the microwave will transfer microwave energy directly to the reactant, so that the interaction of energy from the microwave with the reactant produces effective heating [10].

3.4 Analysis of methyl esters derived from Nyamplung oil

The biodiesel from Nyamplung oil was analyzed by GCMS, The GC Chromatograms and fatty acid compositions of biodiesel are presented in Fig. 3 and Table 5 respectively. The methyl esters composition, chain length and saturation level of oil are important characteristics that indicate the physical state of oil and biodiesel. This characteristic influences cetane numbers and cold flow properties such as cloud point, pour point, cold filter plugging point and cold soak filtration test of biodiesel [21]. The chain length and saturation level affect the density and viscosity of biodiesel. Density increases by decreasing chain length and increasing number of double bonds. While the viscosity increases by increasing chain length and inversely related to the number of double bonds [22].

The GCMS analysis indicate that the biodiesel contained mainly methyl esters of oleic acid (C18:1), linoleic acid (C18:2), stearic acid (C18:0) and palmitic acid (C16:0),

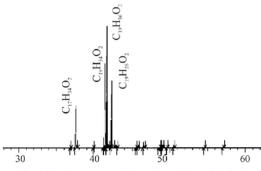


Fig. 3 GC chromatogram of fatty acid methyl ester (biodiesel)

Table 5 FAMEs con	position of synthesi	zed biodiesel
-------------------	----------------------	---------------

Peak no	Retention time (min)	Identified compounds	Molecule formula	%
1	36.84	Methyl oleic	C19H36O2	0.13
2	37.58	Methyl palmitate	C,H _u O,	9.52
3	39.89	Methyl margarate	C18H36O,	0.06
4	41.43	Methyl linoleate	C ₁₀ H _u O,	25.49
5	41.72	Methyl oleic	C ₁₉ H ₃₆ O	44.59
6	42.32	Methyl stearate	C19H38O2	17.70
7	45.86	Methyl heptadec-10-enoate	C 18H 34O,	0.20
8	46.51	Methyl arachidate	C, H, O,	1.14
9	48.53	Methyl heneicosanoate	C22H44O2	0.02
10	50.48	Methyl behenate	C23H46O2	0.34
11	54.57	Methyl tetracosanoate	C25H50O2	0.07

with compositions of 44.72 %, 25.49 %, 17.70 % and 9.52 %. Rashid et al. [12] stated that rice bran biodiesel contained fatty acid consisting mainly of oleic acid, linoleic, palmitate and stearate, respectively 43.1 %, 32.2 %, 18.8 % and 1.4 %.

3.5 Synthesized Biodiesel Physico-chemical properties

The optimum product biodiesel fuel properties result are listed in Table 6. It is observed that this biodiesel obtained from Nyamplung oil in the presence of $BMIMHSO_4$ + NaOH as a catalyst and microwave assisted, fuel properties meets the ASTM D-6751 standards.

Table 6 shows the density biodiesel Nyamplung 868 g/ml. This value is included in ASTM range density biodiesel values between 850 and 894 g/ml. Density is an important parameter in airless combustion system that affect the efficiency of atomization and the content of alkyl ester [23].

High viscosity values will lead to unfavorable atomization of fuel, incomplete combustion and carbon deposition in the injector [23]. The viscosity of Nyamplung biodiesel is 5.878 mm²/s, it meets the national standard up to 6 mm²/s. The acid value of biodiesel provides free fatty acid content in biodiesel and fuel aging rates during storage. The value of this parameter is limited to maximum of 0.8 mg KOH/g and acid value of Nyamplung biodiesel of 0.23 mg KOH/g. The cetane number biodiesel Nyamplung of 70.9, where standard national determine the cetane number of fuel at least 48. The higher cetane number the better ignition and refinement of fuel. Biodiesel has a higher cetane number than fossil fuel, resulting in higher combustion efficiency [23].

Flash point is a parameter that determines the safety of fuel in storage. The high flash point has a fire risk, where

Tabel 6 Synthesized biodiesel physicochemical properties

Tuber o Bynanesized die	areser physic	oenennear prop	serties
Property	Unit	Synthesized biodiesel	ASTM D-6751
Specific Gravity at 60/60 °F	-	0.8782	
Density 15 °C	gr/ml	868	860-894
Kinematic Viscosity at 40 °C	$mm^2\!/\!s$	5.878	1.9-6.0
Flash Point	°C	185	130 min
Color ASTM	-	1.5	-
Water Content	%vol.	Nil	0.030 max
Pour Point	°C	9	-15 to 10
Conradson Carbon Residue	%wt.	0.0021	0.05 max
Gross Heating Value Distillation 90 %	BTU/lb ℃	19404 323	360 max
Acid Value	mgKOH/g	0.23	0.8 max
Cetane number	-	70.9	48 min

the national standard flash point value is specified at least 130 °C. Nyamplung biodiesel has a flash point of 185 °C.

Carbon residue is defined as the amount of carbonaceous matter left after evaporation and pyrolysis of fuel sample under specified condition. Nyamplung biodiesel has a carbon residue of 0.0021 %wt, it meets the national standard. The Nyamplung biodiesel product meets ASTM D-6751 standard.

4 Conclusion

Optimization of the biodiesel production with an ionic liquid + Na H catalyst-assisted microwave have been studied using Response Surface Methodology (RSM) based on Central Composite Design (CCD). Ionic liquid + NaOH catalyst and assisted microwave can improve biodiesel yield. The results showed that the concentration catalyst, the temperature reaction and the molar ratio methanol to oil have a significant effect on the methyl ester yield. The optimum conditions for the transesterification process of Nyamplung (*Calophyllum inophyllum*) oil for 6 minutes are the catalyst concentration of 1.2 %wt, the

References

- Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., Norhasyima, R. S. "Comparison of palm oil, Jatropha curcas and Calophyllum inophyllum for biodiesel: A review", Renewable and Sustainable Energy Reviews, 15(8), pp. 3501-3515, 2011. https://doi.org/10.1016/j.rser.2011.05.005
- [2] Lin, C.-C., Hsiao, M.-C. "Effect of Catalyst Amount, Reaction Temperature and Methanol / Oil Molar Ratio on Conversion Rate of Soybean Oil Assisted by Ultrasonic Mixing and Closed Microwave Irradiation", International Journal of Engineering Inventions, 1(6), pp. 40-48, 2012. [online] Available at: www.ijeijournal.com/papers/ vli6/F0164048.pdf [Accessed: 27 March 2018]
- [3] Lin, Y.-C., Yang, P.-M., Chen, S.-C., Tu, Y.-T., Lin, J.-F. "Biodiesel production assisted by 4-allyl-4-methylmorpholin-4-ium bromine ionic liquid and a microwave heating system", Applied Thermal Engineering, 61(2), pp. 570-576, 2013. https://doi.org/10.1016/j.applthermaleng.2013.08.038
- [4] Fan, M., Huang, J., Yang, J., Zhang, P. "Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst", Applied Energy, 108, pp. 333-339, 2013. https://doi.org/10.1016/j.apenergy.2013.03.063
- [5] Andreani, L., Rocha, J. D. "Use of ionic liquid in biodiesel production: A review", Brazilian Journal of Chemical Engineering, 29(1), pp. 1-13, 2012.

https://doi.org/10.1590/S0104-66322012000100001

[6] Mohammad Fauzi, A. H., Amin, N. A. S. "An overview of ionic liquids as solvents in biodiesel synthesis", Renewable and Sustainable Energy Reviews, 16(8), pp. 5770-5786, 2012. https://doi.org/10.1016/j.rser.2012.06.022 temperature of 71.3 °C and the molar ratio of methanol to oil 10.8 mole/mole to yield 95.8 %. The second order polynomial models were obtained to predict percentage conversion. Validation experiments were also carried out to verify the availability and the accuracy of the model, and the result showed that the predicted value was in agreement with the experimental value. The GCMS analysis indicated that the biodiesel contained mainly of oleic acid (C18:1), linoleic acid (C18:2), stearic acid (C18:0) and palmitic acid (C16:0), with compositions of 44.72 %, 25.49 %, 17.70 % and 9.52 %. The physicochemical properties of Nyamplung Biodiesel have been tested based on the Indonesian National Standard, and the results were in accordance with ASTM D-6751 standard.

Acknowledgement

We gratefully thank Ministry of Research, Technology and Higher Education of Indonesia (Kemenristekdikti) for financial support for the Doctoral Dissertation Project in accordance with the research contract number 1744 / UN37.3.1 / LT / 2017.

- Welton, T. "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis", Chemical Reviews, 99(8), pp. 2071-2084, 1999. https://doi.org/10.1021/cr980032t
- [8] Chen, K.-S., Lin, Y.-C., Hsu, K.-H., Wang, H.-K. "Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system", Energy, 38(1), pp. 151-156, 2012. https://doi.org/10.1016/j.energy.2011.12.020
- [9] El Sherbiny, S. A., Refaat, A. A., El Sheltaway, S. T. "Production of biodiesel using the microwave technique", Journal of Advanced Research, 1(4), pp. 309-314, 2010. https://doi.org/10.1016/j.jare.2010.07.003
- [10] Motasemi, F., Ani, F. N. "A review on microwave-assisted production of biodiesel", Renewable and Sustainable Energy Reviews, 16(7), pp. 4719–4733, 2012.

https://doi.org/10.1016/j.rser.2012.03.069

[11] Perreux, L., Loupy, A. "A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations", Tetrahedron, 57(45), pp. 9199-9223, 2001.

https://doi.org/10.1016/S0040-4020(01)00905-X

[12] Rashid, U., Anwar, F., Ansari, T. M., Arif, M., Ahmad, M. "Optimization of alkaline transesterification of rice bran oil for biodiesel production using response surface methodology", Journal of Chemical Technology and Biotechnology, 84(9), pp. 1364–1370, 2009.

https://doi.org/10.1002/jctb.2191

[13] Patil, P. D., Gude, V. G., Camacho, L. M., Deng, S. "Microwave–
 [18] Meher, L.
 Assisted Catalytic Transesterification of *Camelina Sativa* Oil", esel produ

Energy and fuels, 24(2), pp. 1298-1304, 2010.

- https://doi.org/10.1021/ef9010065
 [14] Hadiyanto, H., Suttrisnorhadi, S. "Response surface optimization of ultrasound assisted extraction (UAE) of phycocyanin from microalgae *Spirulina platensis*", Emirates Journal of Food and Agriculture, 28(4), pp. 227-234, 2016.
 https://doi.org/10.9755/cjfa.2015-05-193
- [15] Sajjadi, B., Aziz, A. R. A., Ibrahim, S. "Investigation, modelling and reviewing the effective parameters in microwave-assisted transesterification", Renewable and Sustainable Energy Reviews, 37, pp. 762–777, 2014.

https://doi.org/10.1016/j.rser.2014.05.021

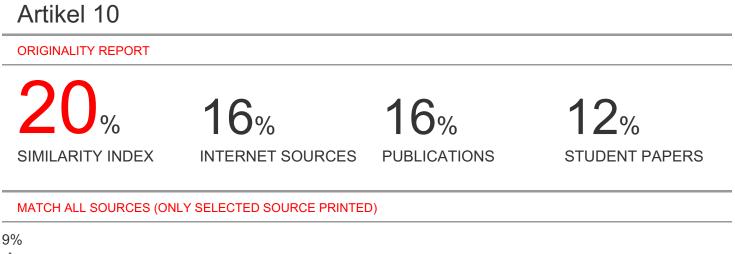
[16] Handayani, P. A., Abdullah, Hadiyanto "Process Evaluation of Biodiesel Production from Nyamplung (*Calophyllum inophyllum*) Oil Enhanced by Ionic Liquid + NaOH Catalyst and Microwave Heating System", Journal of Physical Science, 29(Supp. 2), pp. 265–275, 2018.

https://doi.org/10.21315/jps2018.29.s2.21

[17] Leung, D. Y. C., Wu, X., Leung, M. K. H. "A review on biodiesel production using catalyzed transesterification", Applied Energy, 87(4), pp. 1083–1095, 2010. https://doi.org/10.1016/j.apenergy.2009.10.006 Handayani et al. | 413 Period. Polytech. Chem. Eng., 63(3), pp. 406-413, 2019

- [18] Meher, L. C., Sagar, D. V., Naik, S. N. "Technical aspects of biodiesel production by transesterification – a review", Renewable and Sustainable Energy Reviews, 10(3), pp. 248–268, 2006. https://doi.org/10.1016/j.rser.2004.09.002
- [19] Handayani, P. A., Abdullah, A., Hadiyanto, H. "Biodiesel Production from Nyamplung (*Calophyllum inophyllum*) Oil using Ionic Liquid as A Catalyst and Microwave Heating System", Bulletin of Chemical Reaction Engineering & Catalysis, 12(2), pp. 293-298, 2017. https://doi.org/10.9767/bcrec.12.2.807.293-298
- [20] Gude, V. G., Patil, P., Martinez-Guerra, E., Deng, S., Nirmalakhandan, N. "Microwave energy potential for biodiesel production", Sustainable Chemical Processes, 1(5), pp 1-31, 2013. https://doi.org/10.1186/2043-7129-1-5
- [21] Meher, L. C., Churamani, C. P., Arif, M., Ahmed, Z., Naik, S. N. "Jatropha curcas as a renewable source for bio-fuels — A review", Renewable and Sustainable Energy Reviews, 26, pp. 397–407, 2013. https://doi.org/10.1016/j.rser.2013.05.065
- [22] Mittelbach, M., Remschmidt, C. "Biodiesel: the comprehensive handbook", 1st ed., Martin Mittelbach, Graz, Austria, 2004.
- [23] Enweremadu, C. C., Mbarawa, M. M. "Technical aspects of production and analysis of biodiesel from used cooking oil — A review", Renewable and Sustainable Energy Reviews, 13(9), pp. 2205-2224, 2009.

https://doi.org/10.1016/j.rser.2009.06.007



* Submitted to Higher Education Commission Pakistan

Exclude quotes	On	Exclude matches	< 1%
Exclude bibliography	On		