

Optimization of Transesterification Process of Biodiesel from Nyamplung (*Calophyllum inophyllum* Linn) using Microwave with CaO Catalyst

Heri Septya Kusuma[†], Ansori Ansori, Sasmitha Wibowo, Donny Satria Bhuana and Mahfud Mahfud[†]

Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia

(Received 10 June 2017; Received in revised form 7 June 2018; accepted 22 June 2018)

Abstract – Nyamplung (*Calophyllum inophyllum* Linn) is one of the most widely grown plants in Indonesia. In addition, nyamplung oil has a future competitive advantage in that it can be processed into biodiesel. However, conventional methods for transesterification of nyamplung oil have been less effective. Therefore, in this study biodiesel was produced using microwaves as one of the alternative methods that can improve the shortcomings of conventional methods. In addition, optimization of parameters such as microwave power, catalyst concentration and transesterification time was done using Box-Behnken design. The combination of microwave with CaO catalyst and treated with Box-Behnken design are considered as a new and modern method for production of biodiesel from nyamplung oil and optimizing the factors that affected the transesterification process. The results showed that factors such as microwave power of 449.29 W, concentration of catalyst of 4.86% and transesterification time of 10.07 min can produce optimal yield of biodiesel of 92.73% with reliability of 93.22%.

Key words: Biodiesel, *Calophyllum inophyllum* Linn, CaO, Nyamplung oil, Transesterification

1. Introduction

Population growth and increasing economic development are two factors that cause higher energy demand [1]. Most of the energy used today comes from petroleum, natural gas and coal. Increased energy consumption can lead to depletion of the fuel reserves, which are non-renewable natural resources. Many countries have oil fuel shortages for their own countries. Therefore, it is necessary to look for alternative fuels, especially from renewable materials. One alternative is biodiesel, to replace diesel [2].

Biodiesel is a mono alkyl ester from long chain fatty acids containing 12 to 24 carbon atoms made from renewable lipid sources, such as vegetable oils and animal fats through transesterification [3]. When compared to fossil fuels, biodiesel has advantages, such as raw materials can be renewable, does not have sulfur content so as not to contribute to the occurrence of acid rain, has a very good lubricant properties that can extend the life of the machine, has high flash point so it is safer from fire hazards, can reduce toxic air emissions, and is biodegradable [4].

Nyamplung (*Calophyllum inophyllum* Linn) is one of the most widely grown plants in Indonesia [5]. Some studies on biodiesel development have been done, among others: biodiesel made from palm oil and biodiesel made from raw material of jatropha oil. In addition to oil palm and jatropha oil, the raw material of biodiesel

that has great potential to be developed is nyamplung seed oil.

Compared with fossil fuels, biodiesel has advantages, such as the nature of renewable raw materials, more energy efficiency, can replace diesel fuel, can reduce toxic air emissions, and is also biodegradable [6]. Some of the superiority of biodiesel produced from nyamplung is the yield of nyamplung oil is high compared to other types of plants, jatropha oil 40–60%, palm oil 46–54%, and nyamplung oil 40–73%, and nyamplung seed oil has twice as long compared to kerosene. In addition, nyamplung oil has a future competitive advantage such as biodiesel from nyamplung can be used as a solar mixer with certain composition, even can be used 100% with proper processing technology, better emission quality than diesel, can be used as biokerosene to replace kerosene.

In addition, in this study, innovations were made in the production of biodiesel from nyamplung oil using microwave power. This is because from some previous studies indicating that the use of microwaves in biodiesel production has several advantages, such as enhancing the reaction rate, improving the separation process and can minimize the time of transesterification [7]. While in this research the used catalyst is CaO. The reason for choosing CaO as a catalyst for the production of biodiesel from nyamplung oil using microwave power is that CaO is a heterogeneous catalyst which has properties that are easy to separate with the formed product, requiring no special preparation [8] and has been used by many researchers [9,10]. Therefore, in this study biodiesel from nyamplung oil was produced using microwaves with CaO catalyst, and optimization was done for some parameters such as microwave power, concentration of catalyst and transesterification time using response surface methodology.

[†]To whom correspondence should be addressed.

E-mail: heriseptyakusuma@gmail.com, mahfud@chem-eng.its.ac.id
This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

2. Materials and Method

2-1. Material and process of biodiesel production using microwave

The main raw material used in this study is nyamplung oil and CaO as catalyst. The system consists of domestic microwave oven (EMM2308X, Electrolux, maximum delivered power of 800 W) with wave frequency of 2450 MHz, which is considered as a source of heat for the transesterification process (Fig. 1). On top of that, the system is connected to the reflux condenser used to condense. Holes contained in the microwave serve to connect between the system with condenser which is still open then closed using PTFE. This needs to be done with the aim that the radiation from microwave does not go out into the environment. Finally, the products in the form of biodiesel, which is still mixed with impurities such as glycerol and the remaining catalyst, is separated by separating funnel and washed with warm aquadest (Fig. 2).

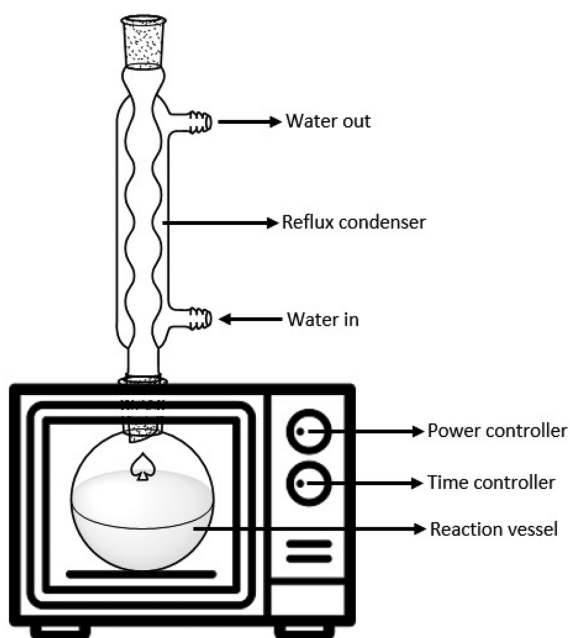


Fig. 1. Schematic representation for transesterification of nyamplung oil using microwave power with CaO catalyst.

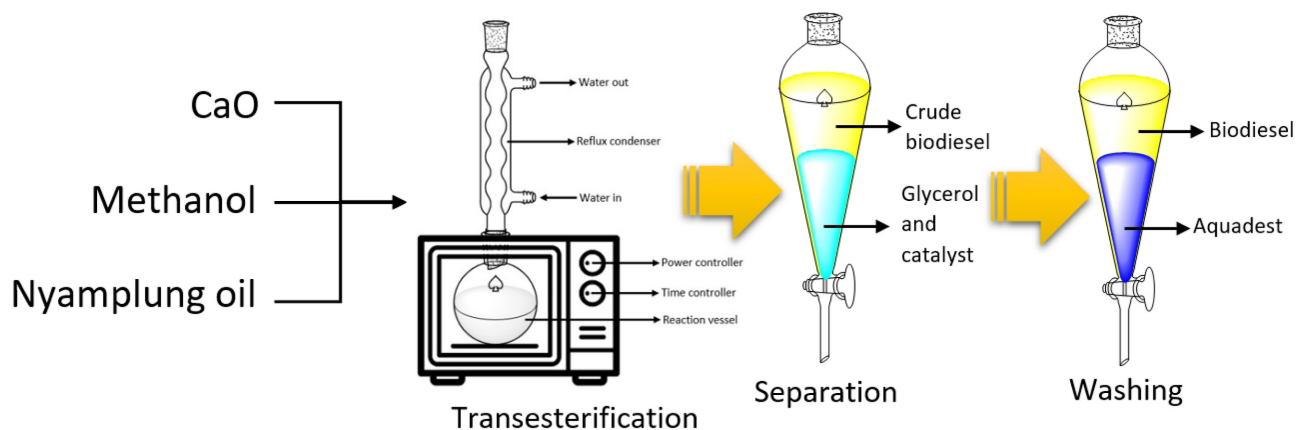


Fig. 2. Experimental procedure for transesterification of nyamplung oil using microwave power with CaO catalyst.

Table 1. Levels of independent variables used for optimization

Levels	Independent factors		
	A (W)	B (%)	C (min)
Minimum point	150	1	10
Central point	300	3	20
Maximum point	450	5	30

2-2. Experimental design with Box-Behnken design

Response surface methodology (RSM) was chosen to optimize the effect factors of transesterification of nyamplung oil on the effect of the microwave power (A), concentration of catalyst (B), and transesterification time (C) to maximize biodiesel yield. Box-Behnken design (BBD) offers the experiment matrix designs, and the response variable is yield of biodiesel obtained (Y), which are displayed in Table 1. The experiment matrix designs were conducted by parameter A set in range of 150-450 W, B set in range of 1-5%, and C set in range of 10-30 min. For the statistical dissect, Design-Expert[®] software version 9.0.4.1 (Stat-Ease Inc., Minneapolis) was practiced to assume the experimental design and to model the data.

3. Results and Discussion

3-1. The effect of microwave power to yield of biodiesel

Microwave power is one of the parameters that needs to be considered, because microwave power affects mass transfer rates. To study the effect of microwave power to yield of biodiesel, then in this research we used some microwave power (150, 300, 450 and 600 W). The effect of microwave power to yield of biodiesel can be seen in Fig. 3.

Based on Fig. 3, higher microwave power can lead to higher yield of obtained biodiesel. This can occur due to the higher temperatures that are in line or proportional to the higher microwave power. The existence of these phenomena has an impact on the increasing efficiency of transesterification process and rate of conversion [11]. In addition, according to Fig. 3 there is also a slight increase in yield between microwave power of 400 to 600 W. So if in this transesterification process using microwave power higher than 600 W it is

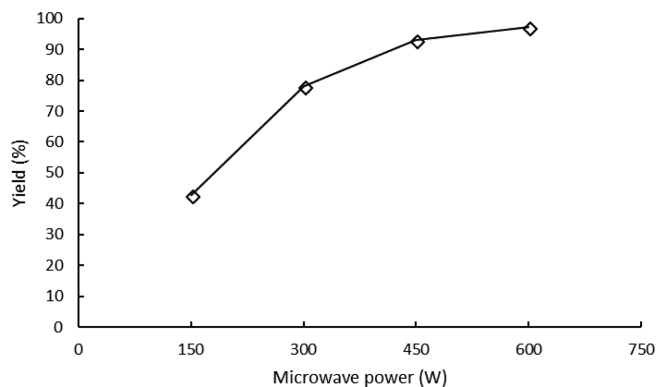


Fig. 3. The effect of microwave power to yield of biodiesel (concentration of catalyst of 5% and transesterification time of 10 min).

feared that yield of obtained biodiesel will become smaller. This is possible because based on previous research too high microwave power can cause the rate of saponification reaction or soap formation from triglycerides become increasing [12].

3-2. The effect of concentration of catalyst to yield of biodiesel

In the transesterification process, the determination of catalyst concentration needs to be considered. In the production of biodiesel through the transesterification process it is necessary to add catalyst with a certain concentration. Too high concentration of catalyst can cause the formation of soap, which is the result of a reaction between triglycerides with catalyst. To study the effect of concentration of catalyst to yield of biodiesel, then in this research we used some concentration of catalyst (0.5, 1.0, 3.0 and 5.0%). The effect of concentration of catalyst to yield of biodiesel can be seen in Fig. 4.

Based on Fig. 4, the higher concentration of catalyst can lead to higher yield of obtained biodiesel. This is in accordance with research by Encinar *et al.* (2012) [13] who reported that a higher concentration of catalyst can lead to higher yield of obtained biodiesel.

3-3. The effect of transesterification time to yield of biodiesel

In addition to microwave power and concentration of catalyst, transesterification time is a parameter that also needs to be consid-

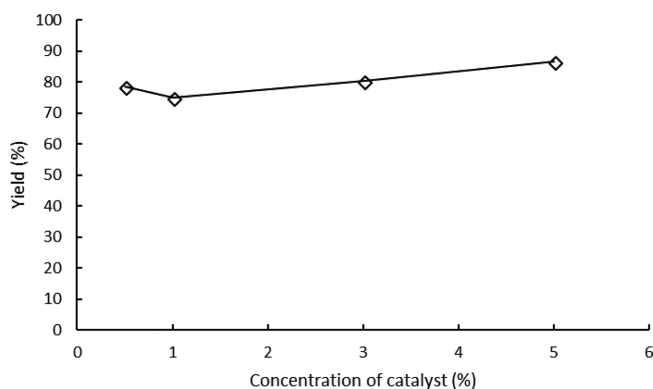


Fig. 4. The effect of concentration of catalyst to yield of biodiesel (microwave power of 300 W and transesterification time of 30 min).

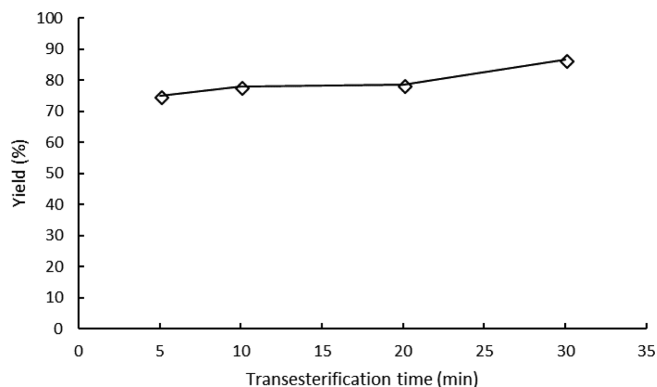


Fig. 5. The effect of transesterification time to yield of biodiesel (microwave power of 300 W and concentration of catalyst of 5%).

ered. To study the effect of transesterification time to yield of biodiesel, we used some transesterification time (5, 10, 20 and 30 min). The effect of transesterification time to yield of biodiesel can be seen in Fig. 5.

Based on Fig. 5, the yield of obtained biodiesel between transesterification time of 5 to 30 min is likely to be constant. This indicates that production of biodiesel is almost reaching equilibrium at transesterification time of 5 to 30 min, and if transesterification is done with longer time it is possible to cause soap formation or saponification reaction. Meanwhile, if transesterification is done with a shorter time, it is possible that the production of mono-glycerides and diglycerides will increase and the production of esters will decrease [14].

3-4. Analysis of Box-Behnken design

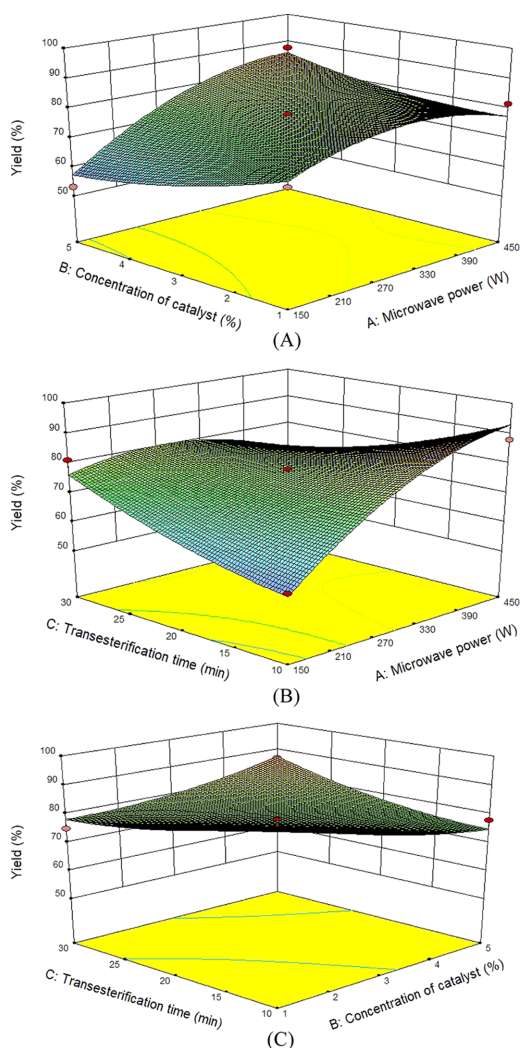
A total of 17 experiments were carried out to estimate the response surface the biodiesel yield. The response variable is that the biodiesel yield (Y) depends on the independent variables realize through the experiments is indicated in Table 2. The results showed that there is a contact between factors biodiesel yield. To determine which of the effects in the model are statistically significant, the p-value of regression was significant with a commonly used α -level of 5% [15-19]. The quadratic model is described by the following as in Eq. (1):

$$\text{Yield} = 48.74 + 0.32*A - 17.54*B + 0.13*C + 0.02*A*B - 0.01*A*C + 0.33*B*C - 3.10^{-4}*A^2 + 0.62*B^2 + 0.03*C^2 \quad (1)$$

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Fig. 6 shows a 3D model of the relationship between the attained biodiesel yield and three independent factors: microwave power (A), concentration of catalyst (B), and transesterification time (C). The result of variance analysis for yield of biodiesel showed R^2 value was 93.22%. This indicates that fixed variables (microwave power (A), concentra-

Table 2. Results of the experimental and model values for production of biodiesel using microwave power with CaO catalyst

Microwave power (W)	Concentration of catalyst (%)	Transesterification time (min)	Yield (%)		Residual (%)
			Experimental	Model	
150	1	20	72.09	73.85	-1.76
150	3	30	81.25	76.27	4.97
150	5	20	53.06	57.33	-4.27
150	3	10	56.16	55.11	1.05
300	3	20	78.10	78.10	0.00
300	3	20	78.10	78.10	0.00
300	1	30	75.10	78.31	-3.21
300	1	10	92.72	92.01	0.71
300	3	20	78.10	78.10	0.00
300	3	20	78.10	78.10	0.00
300	5	30	86.73	87.44	-0.71
300	5	10	78.03	74.82	3.21
300	3	20	78.10	78.10	0.00
450	3	10	87.92	92.90	-4.97
450	3	30	69.60	70.65	-1.05
450	1	20	81.71	77.44	4.27
450	5	20	87.67	85.91	1.76

**Fig. 6. 3D response surface plot showing effect of: (A) microwave power and concentration of catalyst, (B) microwave power and transesterification time and (C) concentration of catalyst and transesterification time.**

tion of catalyst (B), and transesterification time (C)) have an effect of 93.22% on the model. Based on Table 3 it can be seen that microwave power (A), interaction between microwave power and concentration of catalyst (AB), interaction between microwave power and transesterification time (AC), concentration of catalyst and transesterification time (BC) and quadratic of microwave power (A^2) are significant model terms ($p < 0.05$). Optimization results are given with the biodiesel yield of 92.73% with $A = 449.29$ W, $B = 4.86\%$ and $C = 10.07$ min for desirability of 100%.

The model F-value of 10.70 implies the model is significant. There is only a 0.25% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, AB, AC, BC, A^2 are significant model terms. Values greater than 0.10 indicate the model terms are not significant. Analytical results showed that the factors interacted with the essential oil function with significance level $R^2 = 0.93$ and confidence level was 95% as can be seen in Table 3. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. In addition, as observed in Fig. 7, the high correlation coefficient represents a high degree of safety between the actual and predicted values, because most of the points are closely aligned with the straight line. This has proven that the results of the investigations during the transesterification process are accurate and the optimization is highly effective.

4. Conclusion

Under the optimization performed by Box-Behnken design, the conditions for transesterification of nyamplung oil using microwave with CaO catalyst have been suggested as follows: microwave power of 449.29 W, concentration of catalyst of 4.86% and transesterification time of 10.07 min with yield of 92.73%. Box-Behnken

Table 3. ANOVA for quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1595.37	9	177.26	10.70	0.0025
A-Microwave power	517.40	1	517.40	31.23	0.0008
B-Concentration of catalyst	32.51	1	32.51	1.96	0.2041
C-Transesterification time	0.58	1	0.58	0.035	0.8564
AB	156.15	1	156.15	9.42	0.0181
AC	471.11	1	471.11	28.43	0.0011
BC	173.21	1	173.21	10.45	0.0144
A ²	202.81	1	202.81	12.24	0.0100
B ²	25.72	1	25.72	1.55	0.2528
C ²	27.85	1	27.85	1.68	0.2359
Residual	115.99	7	16.57		
Lack of Fit	115.99	3	38.66		
Pure Error	0.00	4	0.00		
Cor Total	1711.36	16			

$R^2 = 0.93$; Adj R-Squared = 0.85; Std. Dev. = 4.07; Mean = 77.21; C.V. (%) = 5.27

References

- Moreau, V. and Vuille, F., "Decoupling Energy Use and Economic Growth: Counter Evidence from Structural Effects and Embodied Energy in Trade," *Appl. Energy*, **215**, 54-62(2018).
- Hassan, M. H. and Kalam, M. A., "An Overview of Biofuel as a Renewable Energy Source: Development and Challenges," *Procedia Eng.*, **56**, 39-53(2013).
- Demirbas, A., "Biodiesel Production from Vegetable Oils by Supercritical Methanol," *J. Sci. Ind. Res. (India)*, **64**, 858-865(2005).
- Huang, D., Zhou, H. and Lin, L., "Biodiesel: An Alternative to Conventional Fuel," *Energy Procedia*, **16**, 1874-1885(2011).
- Fadhullah, M., Widiyanto, S. N. B., Restiawaty, E., "The Potential of Nyamplung (*Calophyllum inophyllum* L.) Seed Oil as Biodiesel Feedstock: Effect of Seed Moisture Content and Particle Size on Oil Yield," *Energy Procedia*, **68**, 177-185(2015).
- Ajala, O. E., Aberuagba, F., Odetoye, T. E. and Ajala, A. M., "Biodiesel: Sustainable Energy Replacement to Petroleum-based Diesel Fuel - A Review," *ChemBioEng Rev.*, **2**, 145-156(2015).
- El Sherbiny, S. A., Refaat, A. A. and El Sheltawy, S. T., "Production of Biodiesel Using the Microwave Technique," *J. Adv. Res.*, **1**, 309-314(2010).
- Boey, P. L., Maniam, G. P. and Hamid, S. A., "Performance of Calcium Oxide as a Heterogeneous Catalyst in Biodiesel Production: A Review," *Chem. Eng. J.*, **168**, 15-22(2011).
- Marinković, D. M., Stanković, M. V., Veličković, A. V., Avramović, J. M., Miladinović, M. R., Stamenković, O. O., Veljković, V. B. and Jovanović, D. M., "Calcium Oxide as a Promising Heterogeneous Catalyst for Biodiesel Production: Current State and Perspectives," *Renew. Sustain. Energy Rev.*, **56**, 1387-1408(2016).
- Colombo, K., Ender, L. and Barros, A. A. C., "The Study of Biodiesel Production Using CaO as a Heterogeneous Catalytic Reaction," *Egypt. J. Pet.*, **26**, 341-349(2017).
- Hsiao, M.-C., Lin, C.-C. and Chang, Y.-H., "Microwave Irradiation-assisted Transesterification of Soybean Oil to Biodiesel Catalyzed by Nanopowder Calcium Oxide," *Fuel*, **90**, 1963-1967(2011).
- Mathiyazhagan, M. and Ganapathi, A., "Factors Affecting Biodiesel Production," *Res. Plant Biol.*, **1**, 1-5(2011).
- Encinar, J. M., González, J. F., Martínez, G., Sánchez, N. and Parda,

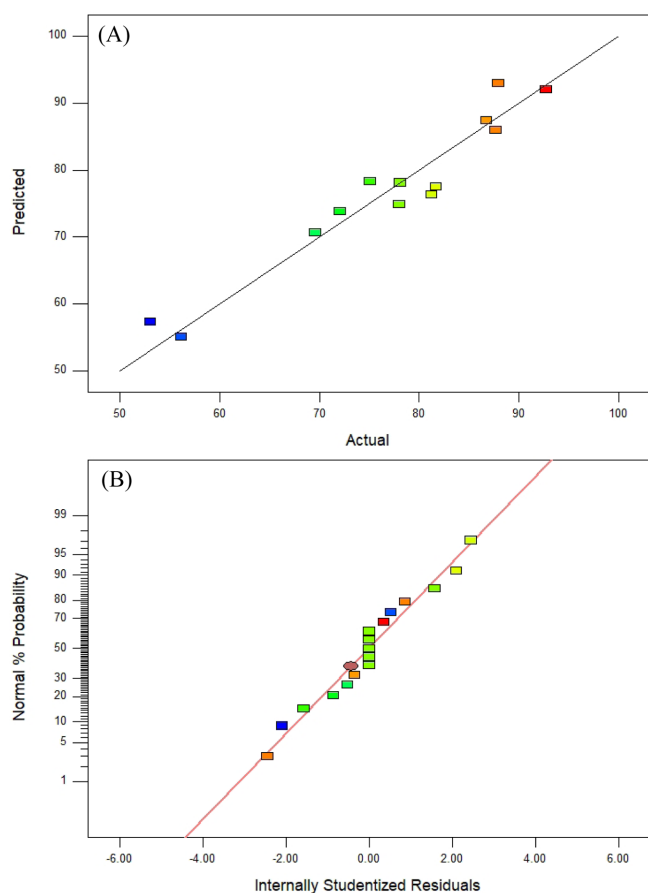


Fig. 7. (a) predicted and experimental yield of biodiesel for 17 experimental conditions and (b) normal residual plot according to the regression model reported in Table 3.

design and transesterification of nyamplung oil using microwave with CaO catalyst showed not only the convenience of the experiments, but also the optimization of the three parameters in detail, which made the yield of biodiesel obtained more efficiently both quantity and quality.

- A., "Soybean Oil Transesterification by the Use of a Microwave Flow System;" *Fuel*, **95**, 386-393(2012).
14. Zhang, S., Zu, Y. G., Fu, Y. J., Luo, M., Zhang, D. Y. and Efferth, T., "Rapid Microwave-assisted Transesterification of Yellow Horn Oil to Biodiesel Using a Heteropolyacid Solid Catalyst;" *Bioresour. Technol.*, **101**, 931-936(2010).
15. Kusuma, H. S. and Mahfud, M., "Response Surface Methodology for Optimization Studies of Microwave-Assisted Extraction of Sandalwood Oil;" *J. Mater. Environ. Sci.*, **7**, 1958-1971(2016).
16. Kusuma, H. S. and Mahfud, M., "Box-Behnken Design for Investigation of Microwave-assisted Extraction of Patchouli Oil;" In: *AIP Conference Proceedings* (2015).
17. Ahmad, A., Alkharfy, K. M., Wani, T. A., Raish, M., "Application of Box-Behnken Design for Ultrasonic-assisted Extraction of Polysaccharides from Paeonia Emodi;" *Int. J. Biol. Macromol.*, **72**, 990-997(2015).
18. Chen, F., Jia, J., Zhang, Q., Yang, L. and Gu, H., "Isolation of Essential Oil from the Leaves of Polygonum Viscosum Buch-ham. Using Microwave-assisted Enzyme Pretreatment Followed by Microwave Hydrodistillation Concatenated with Liquid-liquid Extraction;" *Ind. Crops Prod.*, **112**, 327-341 (2018).
19. Jahirul, M. I., Koh, W., Brown, R. J., Senadeera, W., O'Hara, I. and Moghaddam, L., "Biodiesel Production from Non-edible Beauty Leaf (*Calophyllum inophyllum*) oil: Process Optimization Using Response Surface Methodology (RSM);" *Energies*, **7**, 5317-5331 (2014).