Research Article

Ansori Ansori, Sasmitha Ayu Wibowo, Heri Septya Kusuma*, Donny Satria Bhuana, Mahfud Mahfud*

Production of Biodiesel from Nyamplung (Calophyllum inophyllum L.) using Microwave with CaO Catalyst from Eggshell Waste: Optimization of Transesterification Process Parameters

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Abstract: Fossil fuel is the main energy resource in Indonesia with oil as the dominant fuel (44.1% of primary energy consumption) in 2017. But fossil fuel is not environmentally friendly and non-renewable. Thus, there is a need for alternative renewable fuels such as biodiesel. Biodiesel from nyamplung (Calophyllum inophyllum L.) oil can provide a promising future as a renewable fuel resource. The used of CaO catalyst from eggshell waste is also profitable, and microwave radiation can help the biodiesel production process run more effectively. Optimization of parameters such as microwave power, catalyst concentration, and transesterification time was performed by using Box-Behnken design. Combinations between biodiesel production from nyamplung oil with CaO catalyst using microwave and treated with Box-Behnken design is considered a new and modern method with optimization of the parameters which affect the transesterification process. The result showed that at a microwave power of 325.24 W, a concentration of catalyst of 3.88%, and a transesterification time of 12.47 min can produce an optimal yield of biodiesel of 98.9079% with the reliability of 92.37%.

Keywords: biodiesel; Box-Behnken design; Calophyllum inophyllum L.; eggshell waste; microwave.

1 Introduction

Energy has become one of the most important resources in Indonesia. In 2016, the highest energy consumption came from the transportation sector for 43.89% followed by the industry sector (30.88%), household (16.62%), commercial (5.8%), and others (2.81%). In 2017, energy consumption in Indonesia increased by 5.0%, while the average growth was only 2.9% in the last 10 years. So that in the last 20 years will cause a doubling in energy consumption [1].

Unfortunately, most of the energy needs in Indonesia are still fulfilled by fossil fuels. Where oil remains to be the dominant fuel by 44.1% of primary energy consumption, while for coal of 32.6%, and natural gas of 19.2% [1]. But fossil fuels have some disadvantages, one of them is that it is hard to find new resources when the current resources are decreasing as they are non-renewable. Oil production is increasing (+7.9%) in 2017 for the second consecutive years but had declined from 2011-2015. The coal production from Indonesia increased by 1.3% in 2017 but is still below the 10-year average annual increase of 8.9%. Natural gas production dropped for the seventh year in a row and is now 22% below the 2010 peak [1].

Another disadvantage of fossil fuels is that they are not environmentally friendly. Carbon dioxide (CO2) is a good indicator of the outcome of burning fossil fuels. Besides CO2, there are still other pollutants released from the combustion result. Indonesia’s CO2 emission from energy used increased by 5.5% in 2017 [1].

With those conditions, there is a need for alternative energy resources, one of those is biodiesel. Biodiesel or mono-alkyl esters are renewable fuels that can be produced by reacting alcohol with long-chain fatty acids such as vegetable oils, animal fats, or fatty residues with the addition of catalysts [2]. The use of biodiesel as an energy resource in Indonesia also supported by policies.
Ministry of Energy and Mineral Resources regulation 12/2015 stated that the biodiesel mandatory target in transportation, industry, and electricity sector are each 30%.

Biodiesel is a renewable fuel, biodegradable, a high cetane number and flash point, possesses inherent lubricity, non–toxic, and has less emission compared to fossil fuels. All these qualities make it ideal fuels for the future [3]. Biodiesel has feedstocks derived from 350 available plants and has been identified as potential feedstocks. Feedstocks selection is important in biodiesel production to maintaining lower production costs [2].

Feedstock for biodiesel are divided into edible oil and non-edible oil. Non-edible oil has more advantages than edible oil. They can eliminate rivalry in the food, more efficient, more economical, and more environmentally friendly because non-edible plants, don’t make any damage to vital soil resources, and no deforestation [2].

Calophyllum inophyllum L. nyamplung plant is one of many non-edible plants in Indonesia. Nyamplung plant has high oil content so that huge potential as biodiesel feedstock [4]. The seed kernel of Calophyllum inophyllum L. contains 40–75% dry basis weight of oil [5], which has a higher oil content than Jatropha seed oil (40–60%) and rubber seed oil (40–50%) [2]. The yield of Calophyllum inophyllum L. oil per unit land area was more than 4 t/ha which is much more than yield of Jatropha curcas L. oil (1900–2500 kg/ha) and rubber seed oil (40–50 kg/ha) [2].

Catalyst selection is also an important factor in biodiesel production to get lower of cost production. Calcium oxide (CaO) is one of the heterogeneous catalysts lapsed for the production of biodiesel. Heterogeneous catalysts could restore easily, are reusable, and can minimize the purification process [6]. CaO catalysts can be made through the CaCO3 calcination process. One source of CaCO3 that is easily obtained around us is from eggshells [7]. Calcined eggshells as a catalyst can yield more than 90% FAME in biodiesel production [8].

The selection of energy sources for the process of biodiesel production is very important considering that biodiesel itself is a new energy source. So that the manufacturing process must prioritize the effectiveness of energy use [9]. Microwave is electromagnetic radiation which transfers energy directly to the reactants and raises the intense localized heating [10]. In microwave heating, the energy interacts with reactants on the molecular levels [11]. Therefore, microwave radiation can hasten the reaction rate, reduce reaction time, and escalate the yield of biodiesel [9,10].

Response surface methodology (RSM) was a combination of mathematical and statistical methods that have been successfully used to know the effect of independent variables and optimize complex processes. The main advantage of RSM was to decrease the number of experiments so it requires fewer levels and to evaluate independent variables and their interactions [12–14]. Box-Behnken Design (BBD) was one of many types of RSM that have been greatly used by researchers for the optimization of an experiment. This is because BBD has many advantages, including BBD is not only effective in the optimization of variables with the least number of experiments but also contributes to further analysis of interactions between different variables. Furthermore, it can avoid the combination of treatment in the extreme range and estimate the factor of the quadratic model efficiently [15].

Therefore, in this research, the biodiesel production from Calophyllum inophyllum L. oil using microwave with CaO catalysts from calcined eggshells. The optimization was done for some parameters such as microwave power, concentration of catalyst, and transesterification time by using RSM.

2 Materials and Method

2.1 Catalyst preparation

Chicken eggshells waste were washed and crushed to 40 mesh size. Next, the eggshells were dried at 110°C for 24 hours in the oven. Then, eggshells were calcined for 2.5 hours at 900°C using the furnace.

2.2 Materials and process of biodiesel production using microwave

The main raw material used in this research was crude oil of Calophyllum inophyllum L. obtained from Cilacap area, Central Java, Indonesia in slushy form that was dark green with oil characteristics, in the form of density of 0.9387 gr/mL, viscosity of 53.6259 cSt, and free fatty acid (FFA) levels of 27.9%. Because the level of FFA from crude nyamplung oil is relatively high (> 2%) so that can cause a saponification reaction at the transesterification process, which is the reaction that occurs between FFA and base catalyst [8,16]. Therefore a pretreatment was needed, namely a degumming process and esterification process before proceeding to the transesterification process. The degumming process begins with Calophyllum inophyllum L. oil which is heated at a temperature of 80°C, then
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attended by the addition of 85% phosphoric acid as much as 5% (v/v) with stirring for 15 min using the magnetic stirrer to remove gums from the oil. While the esterification process was carried out to reduce FFA levels by reacting FFA with methanol (oil to methanol molar ratio of 1:40) with the help of pure sulfuric acid catalyst as much as 10% (w/w) at a microwave power of 450 W for 20 min to produce methyl esters. After the FFA level < 2%, then proceeded to the transesterification process. The transesterification process was done by reacting to the oil from the esterification process with methanol (oil to methanol molar ratio of 1:9) and with the addition CaO-eggshell catalyst. This reaction begins with mixing CaO-eggshell and methanol catalysts with heating and stirring for 2 min so that formed a methoxide mixture. Then, the methoxide mixture is put into the reactor which has been filled with heated esterification oil. The reaction was done with constant stirring using a magnetic stirrer on microwave power and the transesterification time depending on variables. The variables used are concentration of catalyst (% (w/w) oil): 1, 2, 3, 4 and 5%; microwave power (W): 150, 300, 450 and 600; and transesterification time (min): 5, 10, 15, 20, 25 and 30. The reactor is using one neck flask Pyrex with a volume of 1000 mL. The system consisted of a domestic microwave oven (EMM2308X, Electrolux, maximum power 800 W) with wave frequency of 2.45 GHz, for heat sources equipped with magnetic stirrers in the esterification and transesterification process (Figure 1). On top of the microwave, there was a hole to connect with a reflux condenser. The hole was enclosed with PTFE to preventing radiation out from microwave. After the reaction was complete, the results of the transesterification were obtained which included a mixture of methyl ester, glycerol, remaining reactants (nyamplung oil and methanol) and catalyst. The CaO-eggshell catalyst used is a heterogeneous catalyst, so it is easily separated by filtering with a vacuum pump. While the mixture between biodiesel and other impurities was separated using a separating funnel and washed with warm aquadest (60°C). After that, the products were dried in the oven at 110°C to reduce water content in biodiesel products. The yield of biodiesel can be calculated with:

\[
\text{Yield (\%)} = \frac{\text{mass of methyl ester}}{\text{mass of crude biodiesel oil}} \times 100\% \quad (1)
\]

2.3 Box-Behnken experimental design

RSM was chosen to approximate and optimize the effects of factors on the transesterification process of Calophyllum inophyllum oil with CaO eggshells catalyst by using microwave. Box-Behnken Design (BBD) was applied to evaluate and optimize the effects of three independent variables and their interactions that influence the response variables, i.e. the yield of biodiesel (Y) obtained. The three independent variables include microwave power (A), concentration of catalyst (B), and transesterification time (C) as shown in Table 1. The experiment matrix design was carried out on the 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 6.0.8 (Stat-Ease Inc., Minneapolis MN 55413) has been practiced to assume the experimental design and to model the data of experiments.

Ethical approval: The conducted research is not related to either human or animal use.

Figure 1: Schematic representation to produce biodiesel of transesterification process of nyamplung (Calophyllum inophyllum L.) oil with CaO catalyst from eggshells waste by using microwave.

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      |

Ethical approval: The conducted research is not related to either human or animal use.
3 Result and Discussion

3.1 Characterization of catalyst using XRD

The main compounds that make up almost all parts of the eggshell are CaCO$_3$, so that heating at high temperatures can decompose CaCO$_3$ into CaO.

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

The eggshell calcination process aims to eliminate the water content, organic compounds, and carbon dioxide contained in the eggshell. Water and organic compounds can generally be removed from eggshells at temperatures below 600°C, while new carbon dioxide can be released from eggshells at temperatures around 700 - 800°C. Therefore, to get a good CaO catalyst from eggshells, the calcination temperature used must be above 800°C [17]. In this study, the calcination process of chicken eggshells was done at 900°C for 2.5 hours.

Characterization results using XRD showed that the compound produced from calcination of chicken eggshells at 900°C for 2.5 hours was CaO. In the diffractogram in Figure 2, shows that the diffraction pattern of eggshell CaO has 2θ peaks which correspond to the character of commercial CaO. In the diffractogram (Figure 2A), peaks appear scattered between angles 2θ (30°-70°) which are characters of CaO (JCPDS No. 00-037-1497). Pattern at 2θ = 32,20°; 32,29°; 37,32°; 37,42°; 37,53°; 53,86°; 54,02°; 64,18°; 64,35°; 67,39°; 67,58°, where at peak 37,42° it has a relatively 100% intensity with a peak height of 1509,1 counts. Whereas in the commercial CaO diffractogram (Figure 2B), the pattern is at 2θ = 34,14°; 54,35°; 62,56°; 64,19°, where at peak 34,14° it has a relatively 100% intensity with a peak height of 672,25 counts. From the peak pattern at 2θ, it is explained that the CaO content in Figure 2A is better than the CaO in Figure 2B because CaO (Figure 2B) reacts with water vapor from the air, so obtained impurity in the form of Ca(OH)$_2$. These results of eggshells calcination are appropriate with research conducted by Khemtong et al. (2012) [10] which uses catalysts from eggshells to produce biodiesel. In addition, research from Wei et al. (2009) [17] is also appropriate because it produces a pattern at 2θ = 32,20°; 37,41°; 53,90°; 64,08°; 67,54°. Based on the diffractogram pattern that occurs, there are high and cramped peaks from eggshells catalyst produced by the calcination process. This shows that there is a good crystalline structure from eggshells catalyst, which especially is composed of active material CaO. The high level of CaO contributes to the efficiency of the transesterification process. These XRD results are appropriate with results of research conducted by Asri et al. (2017) [18] and Buasri & Loryuenyong (2017) [19] which calcined eggshells at 900°C.

In the diffractogram in Figure 2C, shows that the diffraction pattern of the remaining eggshell catalyst used in the transesterification reaction has 2θ peaks that are in accordance with the character of commercial CaO (Figure 2B). From Figure 2C, the pattern at 2θ = 34,08°; 39,44°; 54,41°; 62,55°; 64,42°; 84,75° which shows the formation of CaO compounds, where at peak 34,08° it has a relatively 100% intensity with a peak height of 549,52 counts. Furthermore there is a pattern at 2θ = 17,99°; 28,71°; 29,37°; 47,11°; 48,45°; 50,75° which shows the formation of Ca(OH)$_2$ compounds. The results of characterization using XRD showed that the compounds produced from the remaining catalyst from eggshells that had been used were CaO and Ca(OH)$_2$. This is because the rest of the CaO catalyst (after reaction) can react with water vapor from the air to form Ca(OH)$_2$, compound where the color of the catalyst changes from white to yellow. The formation of the compound Ca(OH)$_2$ cannot be avoided after the transesterification reaction. However, the rest of the catalyst can still be used again because it still contains a lot of CaO. These results of XRD are appropriate with research conducted by Tang et al. (2013) [20] and Sundari et al. (2015) [21] which contained Ca(OH)$_2$, from the catalyst due to CaO hydration.

3.2 The effect of some variables to yield of biodiesel

3.2.1 The effect of microwave power to yield of biodiesel

Microwave power is one of the parameters that need to be considered because microwave power affects mass transfer rates. Power in the transesterification process has an effect on to yield of biodiesel. To study the effect of microwave power on the yield of biodiesel, we used various microwave powers (150, 300, 450 and 600 W). Optimization of the transesterification process needs to be done to decide the best-operating conditions, both in terms of quality and economy. The effect of microwave power to yield of biodiesel can be seen in Figure 3.

Based on Figure 3, higher microwave power (150 W to 300 W) can cause an increase in the yield of biodiesel obtained. However, at a power above 300 W, there is a decrement of biodiesel yield occurs. These are because at a power above 300 W, the reactants heat up faster which causes the methanol to evaporate quickly so that less methanol is in reaction with oil. It shows that microwave
Figure 2: XRD pattern of: (A) CaO eggshell catalyst calcined at 900°C, (B) commercial CaO catalyst, (C) remaining CaO eggshell catalyst.
power has a strong effect on catalyst activity. These are because of the higher of microwave power will produce a thermal effect which indicated with a vast increase in temperature. Besides, if the microwave power is increased, it can also cause further reactions of biodiesel and glycerol produced [22]. So, it can be concluded that 300 W power is more optimal than the other tested powers in this transesterification process. This is consistent with previous research which explains that increasing the reaction temperature outside the optimal level can reduce biodiesel yield because the temperature is too high which in turn increases the reaction rate of soap forming or saponification reaction from triglycerides [23].

3.2.2 The effect of catalyst concentration to yield of biodiesel

The determination of catalyst concentration also needs to be considered in the transesterification process. In the production of biodiesel through the transesterification process, it is necessary to add a catalyst with a certain concentration because the catalyst can accelerate the reaction rate. To study the effect of concentration of catalyst on the yield of biodiesel, we tested concentrations of catalyst at 1, 2, 3, 4 and 5%. The effect of catalyst concentration on the yield of biodiesel can be seen in Figure 4.

Based on Figure 4, the higher of catalyst concentration used, then higher the yield of biodiesel to a certain point (4%), but once the catalyst concentration surpasses 4%, the yield of biodiesel decreases. This is because the more triglycerides in nyamplung oil react with methanol with the help of catalysts to produce more biodiesel. This is consistent with research by Ong et al. (2013) [24] which shows that higher catalyst concentrations can lead to higher yields of biodiesel to a certain point where the addition of catalysts will further reduce the yield of biodiesel. This is because the catalyst concentration that exceeds the optimum concentration will increase the soap forming or saponification reaction so that the yield of biodiesel produced will decrease. Meanwhile, according to Chen et al. (2012) [25], the use of an excess base catalyst will also be included in the organic layer, so that free fatty acids contained in oil can react with an excess base catalyst which causes more gel formation, where biodiesel is dissolved in glycerol which causes biodiesel yield to decrease. For the highest yield of biodiesel of 93.2467%, a transesterification time for 15 min, microwave power at 450 W, and catalyst concentration of 4% were determined to be ideal conditions.

3.2.3 The effect of transesterification time to yield of biodiesel

In addition to microwave power and catalyst concentration, the transesterification time is a parameter that also needs to be considered. To study the effect of transesterification time on the yield of biodiesel, we tested transesterification times of 5, 10, 15, 20, 25 and 30 min. The effect of the transesterification time on the yield of biodiesel can be seen in Figure 5.
Table 2: Results of the experimental and predicted values for production of biodiesel using microwave with CaO catalyst from eggshells waste.

| Microwave power (W) | Concentration of catalyst (%) | Transesterification time (min) | Yield (%) | Residual (%) |
|---------------------|-------------------------------|-------------------------------|-----------|-------------|
|                     | Actual                        | Predicted                      |           |             |
| 150                 | 1                             | 20                            | 87.9619   | 89.8717     | -1.9099     |
| 150                 | 3                             | 30                            | 87.1742   | 86.1998     | 0.9744      |
| 150                 | 5                             | 20                            | 89.3055   | 90.1166     | -0.8111     |
| 150                 | 3                             | 10                            | 97.9083   | 96.1618     | 1.7465      |
| 300                 | 3                             | 20                            | 97.6818   | 97.6818     | 0.0000      |
| 300                 | 3                             | 20                            | 97.6818   | 97.6818     | 0.0000      |
| 300                 | 1                             | 30                            | 93.1004   | 92.1649     | 0.9355      |
| 300                 | 1                             | 10                            | 98.6663   | 98.5030     | 0.1633      |
| 300                 | 3                             | 20                            | 97.6818   | 97.6818     | 0.0000      |
| 300                 | 3                             | 20                            | 97.6818   | 97.6818     | 0.0000      |
| 300                 | 5                             | 30                            | 95.0356   | 95.1989     | -0.1633     |
| 300                 | 5                             | 10                            | 97.5451   | 98.4806     | -0.9355     |
| 300                 | 3                             | 20                            | 97.6818   | 97.6818     | 0.0000      |
| 450                 | 3                             | 10                            | 91.8806   | 92.8551     | -0.9744     |
| 450                 | 3                             | 30                            | 91.4508   | 93.1974     | -1.7465     |
| 450                 | 1                             | 20                            | 91.2673   | 90.4562     | 0.8111      |
| 450                 | 5                             | 20                            | 95.1328   | 93.2229     | 1.9099      |

Based on Figure 5, the yield of biodiesel produced between 5 to 30 min transesterification time increases. This explains that the longer the transesterification time used, the more the reactants converted into products. But if the reaction has reached a reaction equilibrium, then upgrade heating time will not increase yield value but may reduce the yield value because the reaction that occurs in the transesterification process is a reversible reaction. This shows that biodiesel production almost reaches equilibrium at the time of transesterification from 5 to 30 min. If transesterification is carried out in a shorter time, nyamplung oil may not be completely converted so that biodiesel production is reduced. Whereas, if the longer reaction time is performed it can cause a side reaction, namely the saponification reaction [26]. When viewed from the reaction time, this process is much faster (in min) than conventional processes that require time in hours. Whereas in terms of catalysts, heterogeneous catalysts are more easily separated and can be reused [27,28]. A concentration of catalyst of 4%, microwave power at 450 W, and transesterification time for 30 min, yield of biodiesel 93.9234%.

3.3 The checking of statistical analysis and model fitting

One of RSM is BBD that used to analyze various independent variables and their interactions. In this research, we chose BBD because it is easy and can decrease the number of experiments so it requires fewer levels. Experiments have been conducted as many as 17 experiments, in which these experiments are used to approximate of response surface and obtain the optimum yield of biodiesel. The response parameters are that the yield of biodiesel obtained (Y) depends on the independent variables shown in Table 2. The results of this research indicate that there are interactions between variables in producing biodiesel. So in this research it is also necessary to know the variables that can give statistically significant effect [29]. The quadratic equation model is explained by the following as in Eq. (2):

\[
\text{Yield} = 88.5624 + 0.1088*A + 1.0681*B - 0.7887*C - 0.0002*A^2 - 0.3477*B^2 - 0.0020*C^2 + 0.0021*AB + 0.0017*AC + 0.0382*BC
\]
In the transesterification process of biodiesel using microwave with CaO eggshell catalyst, an analysis of variance (ANOVA) is performed to show the important criteria in certifying modeling and identifying important factors and interactions that affect the yield of biodiesel. ANOVA has been widely used by researchers for graphical analysis of data in defining interactions between process and response variables. The significance of the F-value hinge on the number of degrees of freedom (DF) in the model and is shown in the p-value column (credence level of 95%). Especially higher F-value and smaller P-value (Prob >> F), show significant effects. A probability value of p < 0.05 indicates that the interaction of factors is significant so that the experiment may be modeled accurately and effectively with fewer faults [30]. ANOVA analysis results can be seen in Table 3.

Parameters used to designate that the actual data can be evaluated or not with the results of the statistical model shown in Table 3. The results of ANOVA for a yield of biodiesel showed $R^2$ value was 0.9237 and adj-$R^2$ was 0.8256. A high $R^2$ value designates a good precision and correlation between experimental and predicted values so that the higher reliability of the model in predicting the yield of biodiesel. This shows that the fixed variables (microwave power (A), concentration of catalyst (B), and transesterification time (C)) have an effect of 92.37% on the model. Based on Table 3, it may be seen that the F-value of 9.42 for the model, where p-value of 0.0037 (p-value <0.05) so that the model obtained is significant. This shows that the noise that occurs in the model is only about 0.37%. Besides, the quadratic model can analyze and evaluate the interactions of each factor. In this case, the linear term of transesterification time (C), the interaction term of interaction between microwave power and transesterification time (AC), and quadratic term of microwave power (A²) were found to be significant (p <0.05). These shows that C, AC, A² were the main factors that affect the yield of biodiesel. As for the other terms (A, B, AB, BC, B², and C²) indicate the models are insignificant because “Prob> F” values are higher than 0.05, which means that these factors have little effect on yield of biodiesel. The reducing the model term can be done if there are many terms is not significant (not including those needed on espousing the hierarchy), so that you can increase your model [31,32].

“Adequate precision” is used to gauge the signal ratio toward the noise, where the desired value is higher than 4. Whereas the Adeq-Prec value of the model is 9.8924, where this value denotes an adequate signal so that this model can be used for navigating the design chamber. Besides, the relatively low coefficient of variation (1.7181) indicates a higher level of precision and gives better reproducibility

| Source                          | Sum of squares | DF | Mean square | F-value | P-value |
|---------------------------------|----------------|----|-------------|---------|---------|
| Model                           | 222.9420       | 9  | 24.7713     | 9.4167  | 0.0037  |
| A- Microwave Power              | 6.8109         | 1  | 6.8109      | 2.5891  | 0.1516  |
| B- concentration of catalyst    | 4.5348         | 1  | 4.5348      | 1.7239  | 0.2306  |
| C-Transesterification time      | 46.2690        | 1  | 46.2690     | 17.5889 | 0.0041  |
| AB                              | 1.5899         | 1  | 1.5899      | 0.6044  | 0.4624  |
| AC                              | 26.5446        | 1  | 26.5446     | 10.0908 | 0.0156  |
| BC                              | 2.3353         | 1  | 2.3353      | 0.8878  | 0.3775  |
| A²                              | 121.6058       | 1  | 121.6058    | 46.2279 | 0.0003  |
| B²                              | 8.1447         | 1  | 8.1447      | 3.0962  | 0.1219  |
| C²                              | 0.1755         | 1  | 0.1775      | 0.0667  | 0.8036  |
| Residual                        | 18.4140        | 7  | 2.6306      |         |         |
| Lack of fit                     | 18.4140        | 3  | 6.1380      |         |         |
| Cor total                       | 241.3560       | 16 |             |         |         |

$R^2 = 0.9237$; Adj. $R^2 = 0.8256$; Adeq.Prec. = 9.8924; Std.Dev. = 1.6219; PRESS = 294.6241; Mean = 94.4022; C.V. (%) = 1.7181

*P-value < 0.05 were considered to be significant
in conducting experiments. The standard deviation of the model is 1.6219, which shows a good correlation between experimental data and prediction models [29]. Thus, the established model provides accurate and satisfying results for biodiesel production by the transesterification process.

3.4 Response analysis for the interaction of variables to yield of biodiesel

The response surface contour plot was the best means to express the effect of several parameters on the experimental results that were being investigated. The response surface equation contour plot was generated by using Design-Expert software (version 6.0.8) to learn the effects of variable interactions on the yields of biodiesel obtained. The yield of biodiesel from nyamplung oil was affected by microwave power, concentration of catalyst, and transesterification time given in Figure 6.

Figure 6 shows the 2-D and 3-D models of the relationship between the yield of biodiesel achieved by three independent factors: microwave power (A), concentration of catalyst (B), and transesterification time (C). In Figure 6A, when the 2-D and 3-D response surface plot were developed to show the effect of the interaction between microwave power and concentration of catalyst varying to yield of biodiesel whereas fixed transesterification time for 20 min. First, the higher microwave power can make the yield of biodiesel becomes higher, but at too high microwave power, the opposite happens because of the formation of side reactions (saponification reaction). Second, the yield of biodiesel increase with increasing catalyst concentrations to a certain point, which if still added can reduce biodiesel yields obtained. The highest of biodiesel yield occurred in microwave power of 325.24 W and concentration of catalyst of 3.88%.

In Figure 6C, at fixed microwave power (300 W), the concentration of catalyst is higher and transesterification time which is not too long can produce more biodiesel. So that the optimum conditions of the transesterification process in producing biodiesel have been obtained at a concentration of catalyst of 3.88% and transesterification time for 12.47 min.

Therefore, it can be concluded that the optimum point of the three variables is: microwave power = 325.24 W, concentration of catalyst = 3.88%, and transesterification time = 12.47 min. With those variables, the yield of biodiesel is 98.9079%.

3.5 Adequacy checking of the Box-Behnken model

Ordinarily, it is requisite checking for model adequacy as part of model validation in verifying the accuracy of the model and checking the analysis of experimental data. A valid and accurate mathematical model will provide an adequate approach to the actual process. Diagnostic plots of Box-Behnken model adequacy in producing biodiesel by transesterification process is shown in Figure 7. In Figure 7A, checking of the assumption of normality is investigated by using a plot of normal % probability versus studentized residuals. It has been found that experimental values approached along a straight line so that responses were normally distributed and no aberrations of variance are found. Whereas, the plot of actual versus predicted value for the yield of biodiesel is shown in Figure 7B. The existence of data points around the straight line as a whole shows that the value is close between the actual and the predicted value so that the reliability of the model is high in predicting the yield of biodiesel. This proves that the model can improve the good relationship between response variables so that optimization can be applied. Meanwhile, to analyze the splendid fit of the model is indicated by the plot of the experiment runs versus studentized residuals (Figure 7C). Figure 7C shows that all data dots are still in the limit that is between 0 to ± 3. In Figure 7D, there are no unforeseen errors on the model obtained because the values of the all leverage point are still in the range of 0 to 1. Furthermore, Cook’s distance values are still within the specified range (Figure 7E). The plot results in Figure 7 are satisfactory, so that can be deduced that the empirical model is adequate to illustrate the yield of biodiesel from nyamplung oil by response surface methodology [15,26,31].
Conclusion

RSM has been proven effective in approximating and evaluating the effect of three independent variables and their interactions: including microwave power, concentration of catalyst, and transesterification time in the transesterification process of nyamplung oil. Besides, RSM can also predict optimal operating conditions in producing biodiesel. Based on the analysis of variance, it can be concluded that the Box-Behnken design provides a suitable model in simulating and optimizing three independent variables on the transesterification process.

Figure 6: 2-D and 3-D response surface plot showing interactions of: (A) microwave power and concentration of catalyst with fixed transesterification time of 20 min, (B) microwave power and transesterification time with fixed concentration of catalyst of 3%, and (C) concentration of catalyst and transesterification time with fixed microwave power of 300 W.

4 Conclusion

RSM has been proven effective in approximating and evaluating the effect of three independent variables and their interactions: including microwave power, concentration of catalyst, and transesterification time in the transesterification process of nyamplung oil. Besides, RSM can also predict optimal operating conditions in producing biodiesel. Based on the analysis of variance, it can be concluded that the Box-Behnken design provides a suitable model in simulating and optimizing three independent variables on the transesterification process.
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The optimal conditions for the transesterification process of nyamplung oil using microwave with CaO eggshell catalyst have been determined as follows: microwave power of 325.24 W, concentration of catalyst of 3.88% and transesterification time of 12.47 min, to yield of biodiesel of 98.9079%.

*Conflict of interest:* Authors declare no conflict of interest.

Figure 7: Diagnostic plots of Box-Behnken model adequacy.
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