Ultrasound assisted interesterification for biodiesel production from palm oil and methyl acetate: Optimization using RSM

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Abstract. High energy demand in the industrial world and pollution problems caused by the use of fossil fuels causes the need for the latest innovations that will replace the use of non-renewable energy. One of them is the replacement of diesel fuel with biodiesel. At present biodiesel production uses a transesterification reaction which produces a side product in the form of glycerol. However, the presence of glycerol is considered waste and has no economic value so a separation process is needed. So to eliminate the by-product separation process, a new route is used. This route is called interesterification, using methyl acetate instead of methanol which later produces triacetin as a by-product. Triacetin is recognized as an additive in biodiesel which functions as an anti-knocking in diesel engines. In this research, an interesterification study was carried out by ultrasound and a potassium methoxide catalyst was used to increase the reaction rate and the yield of biodiesel. The operating parameters used include the reactant molar ratio of 1:3; 1:6 and 1:9, catalyst concentration 0.5%; 1.0%; and 1.5%, and reaction times 5, 10, and 15 minutes. The parameter optimization is carried out by the central composite design (CCD) method to reduce the number of experiments needed and also to evaluate various variables and their interactions. The optimal operating conditions are the molar ratio of methyl acetate to palm oil of 8.95, catalyst concentration of 1.44%, and interesterification time of 10.03 minutes can produce the yield of biodiesel of 99.66%.

1. Introduction

Energy is one of the most important resources in human activities. The high demand for energy in the industrial world, and the increasing environmental problems caused by the use of fossil fuels [1], have resulted in the need for new innovations that will replace the use of non-renewable energy. One of the innovations is making biodiesel, which will replace diesel fuel and cut the level of environmental pollution. Biodiesel has several advantages over diesel fuel such as renewable, biodegradable, lower harmful emissions, non-toxicity, has a flash-point and a higher cetane number, sulfur-free, and less carbon monoxide gas produced so that biodiesel is fuel alternatives that are more environmentally friendly [2,3]. Over time, expanded the industrial sector will result in deplete fossil fuel reserves in the coming years. So that biodiesel has great potential to replace fossil fuels that can be depleted and make sure sustained energy sources and human development [4]. Because this biodiesel raw material is easy to get and can be renewed.

Usually, vegetable oil, animal oil, and used oil can be used as raw material for making biodiesel. In general, the manufacture of biodiesel prefers vegetable oil, raw materials to be developed, because
vegetable oil is a natural resource that is available in excess and can be renewed. One of the most prospective raw materials for biodiesel is palm oil. In Indonesia, the palm oil production sector has experienced remarkable growth, with annual growth rates greater than 12% for the years 1990 to 2005 [5]. Meanwhile, according to Varqa in Palm Oil Analytics (2017)[6], Indonesia is in the first put in producing palm oil in the world, which amounted to 34,520,000 tons in 2016. This makes palm oil a great potential for further processing into renewable energy.

Biodiesel has been produced commercially through the transesterification reaction of vegetable oil with methanol using a catalyst that produces esters and glycerol. The formation of glycerol, which is a byproduct of the transesterification process, has a real disadvantage in the biodiesel manufacturing process. Because glycerol has no economic value and its existence can be said to be an impurity in biodiesel. So it is necessary to do the separation and washing process to achieve high purity biodiesel products [7–9]. Moreover, the continuous increase in biodiesel production to comply with current legislation has led to higher than acceptable amounts of glycerol being produced. This glycerol can be produced up to 10% (based on the mass of oil) of the biodiesel obtained so that its availability is too abundant in the market which results in lower prices [10]. Therefore, to overcome the glycerol surplus and its separation process, another alternative is used to produce biodiesel without glycerol. This can be done by interesterification reaction (non-alcoholic route) between vegetable oil and methyl acetate as an alkyl group supply with the aid of a catalyst. The use of methyl acetate to replace methanol will produce biodiesel and a byproduct in the form of triacetin, not glycerol [11–14]. Triacetin has a more economic value than glycerol and can be added to biodiesel obtained, because of its mutually soluble nature. Due to its mutually beneficial solubility, the presence of triacetin up to 10% by weight still produces biodiesel fuel that meets the quality standards of ASTM D6451 and EN 14214, and also the mixture has no adverse effect on the final quality of the fuel and the combustion process in the engine [15–17]. The product advantage of the interesterification process is biodiesel with triacetin as a byproduct which can be used as a fuel additive so there is no need for a byproduct separation process. In addition, this interesterification process provides a shorter reaction time when compared to other processes [12,17].

The interesterification process has been widely studied with enzyme catalysts [18–20] or without a catalyst under supercritical conditions [4,21–23]. However, these two methods have several drawbacks, including the enzymatic route associated with high production costs [24], and the difficulty of producing biodiesel on a large scale because of the need for careful control of the reaction parameters as well as the slow reaction [25]. While the shortcomings of the supercritical method are related to operating conditions, namely very high pressure (10-30 MPa) and high temperature (300-345°C), which increases the cost of heating and evaporation of unreacted methyl acetate [22]. Therefore, another method is used with low operating conditions so that the operating costs are lower than the supercritical method and the reaction time is shorter than the enzymatic method [12,13,26]. The method is chemical interesterification using chemical catalysts. Several chemical catalysts such as potassium methoxide, potassium hydroxide, and polyethylene glycolate have been investigated [11–13]. According to Casas et al. (2013)[26], who have investigated the interesterification of sunflower oil and methyl acetate with a mixture of methanolic potassium methoxide catalyst using a molar ratio of 1:48 and a concentration of catalyst of 1%, resulting in methyl esters of 77.0% (wt) and triacetin of 12.1% (wt), so it can be concluded that the potassium methoxide catalyst gives better results than the others.

To increase the yield of biodiesel and the interesterification rate, the ultrasound method was used in this study. The application of ultrasound can provide a level of process intensification based on cavitation phenomena that can help in mixing the reactants well due to the presence of microturbulence. The cavitation effect can increase mass transfer under low reaction conditions (temperature and pressure) so that it will produce a faster reaction rate with the possibility of reactant molar ratio and lower catalyst concentration and produce more biodiesel in a shorter time [9,27]. According to Maddikeri et al. (2013) [13], production of biodiesel using ultrasound provides a significant increase in yield and lower methyl acetate needs compared to conventional techniques. Furthermore, research conducted by Subhedar and Gogate (2016) [19], also uses ultrasound in producing biodiesel from cooking oil waste by enzymatic interesterification process, resulting in an increase in yield of 6.7% when compared with conventional techniques. Therefore, the use of ultrasound can reduce the reaction time,
molar ratio needs, and lower catalysts with high yields. Meanwhile, to optimize the operating parameters of the reaction, a statistical approach is used, namely the response surface methodology (RSM). RSM is used to reduce the number of experimental trials required and also to evaluate multiple factors and their interactions. Central Composite Design (CCD) is one of the methodologies used to choose the optimum experimental conditions that require a fewer number of experiments to get the right results. In this experiment, CCD with three independent variables was used to determine the effect of the molar ratio of methyl acetate to palm oil, concentration of catalyst, and interesterification time to produce biodiesel [28,29].

2. Materials and Method

2.1 Material and chemicals

The palm oil used as a raw material in this study is the Bimoli brand palm oil obtained from supermarkets. Methyl acetate in the form of pure analysis (Merck KGaA, 99%) obtained from a chemical supplier UD. Sumber Ilmiah Persada in Surabaya. Methanol is the form of pure analysis (Merck KGaA, purity 99.9%) obtained from PT. Kurniaya Multisentosa. Whereas potassium hydroxide (99%) was obtained from Merck KGaA and phosphoric acid (ortho, 85%) and were used as received.

2.2 Catalyst production

Production of catalyst carried out by adding KOH to methanol with a specific ratio through a chemical reaction which can be represented as follows:

\[ \text{CH}_3\text{OH} + \text{KOH} \rightarrow \text{CH}_3\text{OK} + \text{H}_2\text{O} \]

After the reactants were mixed, it was heated by using a heating mantle until the temperature reaches 50-60°C. After that, the product was cooled to room temperature, then the cooled product was separated by distillation to remove excess methanol from the product. Thereafter, the distilled product (bottom product) was heated in an oven (oven temperature around 110°C) to remove the moisture content from the product because the product is a hygroscopic substance [30].

2.3 Equipment and process of biodiesel production using ultrasound-assisted interesterification

The main equipment for the interesterification process is an ultrasonic cleaning bath and a reflux device. The ultrasonic cleaning bath used is KRISBOW model KW1801033, has a voltage of 240V/50 Hz, a power of 100 W, a maximum frequency of 40 kHz, a tank capacity of 2.8 L for heat sources in the interesterification process. Meanwhile, the reflux device consists of a 1000 mL three-neck Pyrex round bottom flask, a 40 cm reflux condenser, and a thermometer to determine the temperature of the interesterification reaction. The interesterification process was carried out by adding palm oil and methyl acetate in a triple neck flask with the ratio (mol/mol) mentioned in the experimental variable. After that, the reactants are heated to 50°C, then the catalyst is added to the flask according to the variable and moves the flask to an ultrasonic-assisted interesterification device (Figure 1), then an interesterification reaction occurs. Ultrasound is injected into the reactants through the flask by a device with a frequency of 40 kHz with certain reaction time. After the reaction is complete, 0.1 mL of phosphoric acid is added to stop the reaction. Then the product mixture is transferred to a separating funnel and washed with 20 mL warm water to remove impurities such as residual methyl acetate and catalyst from the product. The funnel was agitated by shaking and left until it forms two layers. The top layer is transferred to a beaker, then heated by an oven at 110°C to separate the volatile substances from the product. Further, analysis of the products obtained.
2.4 Optimization of biodiesel production

A Central Composite Design (CCD) is one of the response surface methodologies used to select the optimum experimental conditions that require a fewer number of experiments in order to get appropriate results. In this experiment, a central composite design with three independent variables was applied to find the influence of the molar ratio of methyl acetate to oil (A), catalyst concentration (B), interesterification time (C) toward biodiesel yield. A total of 19 experiments were executed with 5 times repeated variable (center point variable) and it was found to be sufficient to calculate the coefficients of the second-order polynomial regression model for the three variables. Each variable was investigated at five levels: -α, -1, 0, +1, and +α. Where the value in parameter A is between 3:1; 6:1; 9:1 (mol/mol), B is defined as 0.5; 1; 1.5% (w/w), and C is set between 5; 10; 15 minutes. The behavior of the yield of biodiesel is explained by the following empirical second-order polynomial model (1):

\[
Y\% = A_0 + A_{1X_1} + A_{1X_2} + A_{1X_3} + A_{2X_1} + A_{2X_2} + A_{2X_3} + A_{3X_1} + A_{3X_2} + A_{3X_3} + A_{12X_1^2} + A_{12X_2^2} + A_{12X_3^2} + A_{13X_1^2} + A_{13X_2^2} + A_{13X_3^2} + A_{23X_1^2} + A_{23X_2^2} + A_{23X_3^2} + A_{33X_1^2} + A_{33X_2^2} + A_{33X_3^2}
\]

Here, Y is the biodiesel’s yield in % and is calculated as follows:

\[
Y\% = \frac{\text{yield}_F - \text{yield}_0}{\text{yield}_0}
\]

Where \(A_0\) is the interception coefficient, \(A_{ij}\), \(A_{ij}^2\), and \(A_{ijk}\) are the interaction coefficients, \(A_{ii}\), \(A_{ij}\), and \(A_{ijk}\) are the quadratic terms, and \(X_i\), \(X_j\), and \(X_k\) are independent variables that influenced biodiesel’s yield (molar ratio, concentration of catalyst, and interesterification time) [31]. For \(\text{yield}_0\) and \(\text{yield}_F\) are the yield of biodiesel in the beginning and in the end of reaction, respectively.

3. Results and Discussion

3.1 Production of biodiesel using ultrasound-assisted interesterification

The biodiesel yield was analyzed by calculating the mass production and divided by fatty acid methyl ester (FAME) produced theoretically. Based on GC-MS (Gas Chromatography-Mass Spectroscopy), the components contained in Bimoli were dominated by palmitic acid (38.201%) and oleic acid (45.962%). From the calculation, it was concluded that the molecular weight of the oil was 850.32 g/mol [32]. Then for FAME produced theoretically was calculated by estimation of reaction stoichiometry.
Figure 2. Interesterification stoichiometry [13]

All reaction products are based on the limiting reactants given. So, if one mole of triglycerides and three moles of methyl acetate were given. Triglyceride was being limited in this reaction. Then theoretically would produce three moles of FAME. Then convert FAME mol to mass value by multiplying with FAME molecular weight. FAME molecular weight was estimated by calculation using equation (3):

\[
MW_{\text{of FAME}} = \frac{(MW_{\text{of methyl palmitate}} + MW_{\text{of methyl oleate}}) - (MW_{\text{of H}}) + (MW_{\text{of C}}) + 3(MW_{\text{of H}})}{3}
\]  

(3)

The calculation above was based on the FAME molecular form the theoretical. The yield analyzed are showed in Table 1.

3.2 Optimization of biodiesel production by response surface methodology (RSM)

A Central Composite Design (CCD) was applied to evaluate the effects of three independent variables (molar ratio of methyl acetate to palm oil (A), catalyst concentration (B), and interesterification time (C)) on the biodiesel production. CCD is one of the Response Surface Methodology (RSM) that used to reduce the number of experimental trials required to evaluate various variables and their interactions. After entering each factor value in the Design-Expert® software version 6.0.8 (Stat-Ease Inc., Minneapolis MN) by selecting CCD so that the experimental design was obtained as many as 19 experiments to obtain the optimum biodiesel yield from palm oil using the ultrasound-assisted interesterification (UAI) method which can be seen in Table 1. In addition, in Table 1, it can also be seen that the yield predicted and actual biodiesel obtained by the UAI method. The results of this study indicate that there is contact between the factors that produce biodiesel. To determine which effect in the model is statistically significant [29,33]. The quadratic polynomial equation model can be used to predict the yield of biodiesel obtained to match the experimental response. Based on the experimental design that has been done, the yield of biodiesel produced using the UAI method can be seen in the quadratic equation as follows (4):

\[
\text{Yield (\%)} = -2.35635 + 10.69713*A + 31.93101*B + 1.814258*C - 0.73129*A^2 - 19.7596*B^2 - 0.11955*C^2 + 3.10583*AB + 0.059284*AC + 0.574748*BC
\]

(4)

Table 1. Response surface central composite design and result for biodiesel production
In the manufacture of biodiesel from palm oil and methyl acetate using the ultrasound-assisted interesterification method, ANOVA analysis was carried out to identify important factors and interactions that influence biodiesel yield using the UAI method. The results of the analysis of ANOVA can be seen in Table 2. An important factor affecting biodiesel yield is indicated by a p-value of less than 0.05.

**Table 2. Analysis of variance for the fitted models**

| Source | Sum of Squares | DF | Mean Square | F-Value | p-value Prob > F |
|--------|----------------|----|-------------|---------|-----------------|
| Model  | 5928.699       | 9  | 658.7443    | 10.2015 | 0.0010          |
| A      | 3882.49        | 1  | 3882.49     | 60.1253 | < 0.0001        |
| B      | 962.972        | 1  | 962.972     | 14.9128 | 0.0038          |
| C      | 42.73655       | 1  | 42.73655    | 0.66183 | 0.4369          |
| A²     | 591.2979       | 1  | 591.2979    | 9.15696 | 0.0143          |
| B²     | 333.1007       | 1  | 333.1007    | 5.15698 | 0.0493          |
| C²     | 121.9233       | 1  | 121.9233    | 1.88814 | 0.2027          |
| AB     | 173.6313       | 1  | 173.6313    | 2.6889 | 0.1355          |
| AC     | 6.326244       | 1  | 6.326244    | 0.09797 | 0.7614          |
| BC     | 16.51678       | 1  | 16.51678    | 0.25578 | 0.6252          |
| Residual | 581.1602   | 9  | 64.57335    |         |                 |
| Lack of Fit | 318.2262   | 5  | 63.64524    | 0.96823 | 0.5272          |
| Pure Error | 262.934  | 4  | 65.73349    |         |                 |
| Cor Total | 6509.859  | 18 |             |         |                 |

Based on Table 2., it can be seen that the model has an F-value of 10.2015 implying that this model is significant because the p-value is less than 0.05. There is only a 0.10% chance that an F-value of this size could be due to noise. In addition, the quadratic model can evaluate and analyze the interaction of each factor. In this case, the independent parameters, namely the molar ratio of methyl acetate to palm oil (A), concentration of catalyst (B), and quadratic parameters, namely the molar ratio of methyl acetate to palm oil (A²) and concentration of catalyst (B²) have an influence of significant on biodiesel yield by using the ultrasound-assisted interesterification method because it has a p-value <0.05.
This shows that A, B, A², B² are the main factors affecting biodiesel yield. Whereas the other parameters (interesterification time (C), the interaction between the molar ratio of methyl acetate to palm oil and concentration of catalyst (AB), the molar ratio of methyl acetate to palm oil and interesterification time (AC), concentration of catalyst and interesterification time (BC), and quadratic parameters of interesterification time (C²)) indicate an insignificant model term because the p-value is greater than 0.05, which explains that these factors less influence the interesterification process of biodiesel. In addition, a Lack of fit is applied to measure the adequacy of the model. Lack of fit has an F-value of 0.97, which implies that the lack of fit is not significant because the p-value is greater than 0.05. The insignificant lack of fit indicates that the model is logical and valid [29,34]. This shows that the model is accurate enough to predict any combination of independent factors in the study range.

Normally, it is necessary to check adequacy as part of model validation in checking the analysis of experimental data and verifying the accuracy of the model. The accuracy or quality of the model can be evaluated using the coefficient of determination (R²). The model obtained in equation (4) has an R² value of 0.9107, this indicates that the proposed model explains 91.07% of the variability in response (experimental values) can be explained by the model. A high value of R² indicates a very nice correlation between experimental and predictive response values so that the reliability of the model is high in predicting biodiesel yield. In addition, the value of adeq precision (11.4025) is greater than 4 which indicates adequate signal and model and can be used to navigate further designs. This proves that the model is very nice and can improve the relationship between the process parameters on the response so that optimization can be applied [28,33].

In this experiment, to examine the influence of several parameters on the response in the form of biodiesel yield using the ultrasound-assisted interesterification method, it can be seen from the graphical representation known as a contour plot. Where this contour plot is obtained from the regression model obtained from equation (4) and is shown in Figure 3.

![Figure 3](image-url)

**Figure 3.** 2-D and 3-D Response surface plots showing the effect of: (A) Interestetration time (10 min), (B) Catalyst concentration (1% w/w), (C) Ratio of methyl acetate to palm oil (6:1)
The contour plot shown in Figure 3A shows the influence of molar ratio and catalyst concentration at fixed interesterification time (10 minutes). An increase in the molar ratio of reactants and catalyst concentration would make more the yield of biodiesel, theoretically. Little difference was shown in Figure 3B, an increase in the interesterification time, did not make a significant difference to the biodiesel produced. Meanwhile, Figure 3C shows the effect of catalyst concentration and interesterification time on a fixed molar ratio (6:1). Increasing the catalyst concentration and interesterification time would theoretically make more biodiesel yield. From the optimization process, variables are produced which theoretically will produce the most optimum results. The optimum conditions for obtaining a yield of biodiesel of 99.66%, in the interesterification process of palm oil with methyl acetate using the UAI method with CCD, are the molar ratio of methyl acetate to palm oil of 8.95:1, catalyst concentration of 1.44%, and interesterification time of 10.03 minutes.

3.3 Adequacy check of the model

Normally, it is necessary to check adequacy as part of model validation in checking the analysis of experimental data and verifying the accuracy of the model. The residual and effect designs for experimental data on the interesterification process are shown in Figure 4. Pareto is used to determine what factors have a significant or no effect on response (Figure 4A). This is indicated by the standardization value of each variable if it is greater than or equal to the standardization value (2.262) so that it can be said to be significant. In addition, Figure 4A also shows the sequence of the most significant variables. In contrast, Figure 4B shows a plot of normal probability versus studentized residuals which can explain that the responses were normally distributed. This is because the experimental values lie linearly on a straight line so that there is no response transformation and no variance deviation. The actual data plot of the predicted value is shown in Figure 4C. This actual data is the initial result data obtained from the experiments conducted (Table 1), while the predicted value is obtained from the equations in the model. The presence of data points in the vicinity of a straight line indicates that the value is close to the predicted and the actual value. This proves that the model can improve the relationship between process parameters in the response so that optimization can be applied. Figure 4D shows the relationship between studentized residuals versus predictions for the interesterification process. It can be seen that the variance is constant for all response values. This is shown by the distribution of points scattered randomly around the boundary between 0 and ± 3 based on the plot in Figure 4D. The plot results in Figure 4, are satisfactory so that it can be concluded that the empirical model is suitable for describing and optimizing the interesterification process [8,28,33,34].

Figure 4. Diagnostic plots for central composite model adequacy
4. Conclusion
In this study, the experimental conditions were optimized by observing the effects of interactions between independent variables on the interesterification reaction using the response surface methodology (RSM). Central Composite Design (CCD) has been proven effective in estimating the effects of three independent variables: molar ratio of methyl acetate to palm oil, catalyst concentration (weight%), and interesterification time (min) on biodiesel production to predict optimal operating conditions. The experimental results show that the linear requirements of the three independent variables have a significant effect on the response value. Based on the analysis of variance, the experimental results indicate that the linear terms of the two independent variables (molar ratio of methyl acetate to palm oil and catalyst concentration) have a significant effect on biodiesel yield. Therefore, it can be concluded that the resulting model is suitable for simulating biodiesel production with a combination of variables tested. The optimal conditions for the interesterification reaction using ultrasound are as follows: the molar ratio of methyl acetate to palm oil of 8.95:1, the catalyst concentration of 1.44%, and the in-situ interesterification time of 10.03 minutes with the maximum predicted yield of biodiesel obtained at 99.66%.

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