Modeling and optimization of palm oil moisture loss as biodiesel pretreatment

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Abstract. One solution to the problem of energy that can be used as a substitute for fuel oil is biodiesel. Palm oil can be used as biodiesel raw material. The advantage of palm oil is its sustainable availability. However, the water content of palm oil still cannot meet the biodiesel quality requirements based on ASTM D975-08a and ASTM D6751-12 which is less than 0.05%. The purpose of this study is to model and optimize the concentration of zeolite and adsorption times to decrease water content in palm oil. The method in this research is to use activated zeolite adsorption. Data from the results of water loss in palm oil as a pretreatment in the manufacture of biodiesel will be processed using response surface methodology (RSM) with the central composite design (CCD) so that a model and optimum point of zeolite concentration and adsorption time can be found. The model produced using the response surface methodology (RSM) method with a central composite design (CCD) design in the form of quadratic equations. The optimization results produce an optimum value of water loss of 2.74% with an error rate of 4.20%. This optimum value is achieved by zeolites concentration of 13.20% and adsorption time of 126.11 minutes.

1. Introduction

The depletion of reserves of fossil fuel sources, especially petroleum, forced the search for alternative fuels as energy sources. One solution to the problem of energy that can be used as a substitute for fuel oil is biodiesel. Biodiesel is an alternative fuel made from renewable plant and animal oils. Indonesia has potential raw materials to produce biodiesel, including palm oil, jatropha, algae, and coconut oil [1]. Biodiesel can be synthesized through the esterification of free fatty acids or transesterification of triglycerides from vegetable oil with methanol to produce methyl esters [2]. Some of these types of materials, palm oil is commonly found and have relatively affordable prices. The advantage of palm oil is its sustainable availability. Palm oil as an affordable material has problems in the transesterification process because the water content in the oil is also still unable to meet biodiesel quality requirements based on ASTM D975-08a and ASTM D6751-12 which is less than 0.05% [3]. While the water content of palm oil on the market is still around 0.3%.

Water content is the percentage of the water content of a material that can be expressed based on wet weight (wet basis) or based on dry weight (dry basis) [4]. High water content in palm oil can cause a burning heat, foaming, and corrosive when reacting with sulfur because it forms acid and gives room for microbes to grow. So that it will become a biodiesel impurity [5]. The value of high-water content in palm oil must be minimized. Besides being an impurity on biodiesel, the high water content in oil will also cause a hydrolysis process where the water contained will react with triglycerides in palm oil.
Water that reacts with triglycerides will produce glycerol which is a by-product of biodiesel so that the biodiesel produced is less than the maximum.

The adsorption process using natural zeolites can be used to reduce water content in cooking oil. Zeolite is a material that has a very regular crystal shape with cavities that are interconnected in all directions and makes the surface area of zeolite very large so it is best used as an adsorbent [6]. Synthetic zeolites or natural can absorb in large enough quantities even at low concentrations. Specifically, for adsorption dryers, zeolites also have a high affinity for water vapor [7] and absorb water by releasing high latent absorption heat [8].

This study aims to model and find the optimum point of zeolite concentration and adsorption time on water content loss in the biodiesel pretreatment by using palm oil. Modeling is needed to explain the relationship between input and output. While optimization is needed to get good results i.e. the right input combination to produce the optimal output [9-11]. The data is modeled using response surface methodology (RSM) so that the optimum zeolite concentration and adsorption time can be found.

2. Methods

This research was conducted at the Basic Chemistry Laboratory, Faculty of Agricultural Technology, Brawijaya University, Indonesia. The tools used in this study include: Beker Pyrex 500 ml to measure the volume and container of the adsorption process, Philips blender to reduce the size of natural zeolite, 100 mesh filter to filter and uniform the size of natural zeolite, heat-resistant container as a container in the process of heating and drying, hot plate magnetic stirrer as a source of heat and stir in the adsorption process, Mettler PM460 digital balance to measure the mass of material, oven Red LINE by Binder RE-53 (230V) as a heat source for the drying process, desiccator as a heat absorber after being roasted, and Design Expert 10.0.3 as data processing software. While the materials used in this study include: Palm oil, natural zeolite obtained from Duta Jaya Labware, Indonesia as an adsorbent, 2 M H3PO4 obtained from Duta Jaya Labware, Indonesia as material for the activation process of natural zeolite, and aquades as material for dilution.

Prior to this research, previous studies had been carried out to observe water content loss in palm oil using zeolite concentration and adsorption times. The ratio of zeolite concentration used is 1: 5, 1:10, and 1:15 and the adsorption time used is 60, 90, and 120 minutes. Based on the preliminary research, the greatest water content loss occurs in zeolite concentration with a ratio of 1:10 and 120 minutes of adsorption time. Therefore, the result from the preliminary study determines the optimum point of the research variables i.e. adsorption time of 150 minutes and the zeolite ratio of 1:10.

3. Results and discussion

Based on Table 1, the results of the water content loss show that the lowest value of the water content loss is 13.335% of zeolite concentration and 77.5736 minutes of adsorption time which results in water content loss value of -3.18%. There are three results of the water content loss which is negative or experiencing an increase in water content. Desorption is the event of releasing material that has been absorbed by the adsorbent. A decrease in adsorption is indicated due to desorption or detachment from the adsorbent caused by weak interactions that occur between ions and adsorbents to bind to the surface of the adsorbent [12]. Absorption or adsorption is an equilibrium process because the rate of adsorption events is also accompanied by the occurrence of desorption events [13]. If the active area of the adsorbent on the inner surface and the outer surface of the adsorbent is full then the adsorption process will not occur again and can actually occur desorption events [14]. Factors that influence the desorption process include temperature, eluent type, the duration of the process and type of adsorbent used [15]. The desorption process in zeolites begins with the heating process. Water is pushed from the zeolite in the form of steam, condenses in containers, where it is stored for re-evaporation. This sequence of processes is completely reversible and can be repeated many times [16]. Water condensing in the container can increase the amount of oil-water content. So that the water content after adsorption has increased. While the highest water content loss is 13.335% of zeolite concentration and 120 minutes of adsorption time which results in a water content loss value of 3.42%.
Table 1. Research results on Design Expert 10.0.3.

| Std | Run | Factor 1 Zeolite concentration (%) | Factor 2 Adsorption time (minute) | X1 | X2 | Response 1 Water content loss (%) |
|-----|-----|----------------------------------|----------------------------------|----|----|----------------------------------|
| 1   | 13  | 6.67                             | 90                               | -1.00 | -1.00 | 1.62                            |
| 2   | 12  | 20                               | 90                               | 1.00 | -1.00 | -1.92                           |
| 3   | 8   | 6.67                             | 150                              | -1.00 | 1.00  | 0.32                            |
| 4   | 9   | 20                               | 150                              | 1.00 | 1.00  | -0.86                           |
| 5   | 3   | 3.90927                          | 120                              | -1.41 | 0.00  | 1.62                            |
| 6   | 4   | 22.7607                          | 120                              | 1.41 | 0.00  | 1.32                            |
| 7   | 1   | 13.335                           | 77.5736                          | 0.00 | -1.41 | -3.18                           |
| 8   | 7   | 13.335                           | 162.426                          | 0.00 | 1.41  | 1.16                            |
| 9   | 11  | 13.335                           | 120                              | 0.00 | 0.00  | 2.68                            |
| 10  | 2   | 13.335                           | 120                              | 0.00 | 0.00  | 1.60                            |
| 11  | 6   | 13.335                           | 120                              | 0.00 | 0.00  | 3.42                            |
| 12  | 10  | 13.335                           | 120                              | 0.00 | 0.00  | 2.22                            |
| 13  | 5   | 13.335                           | 120                              | 0.00 | 0.00  | 3.42                            |

The selection of statistical models [17] based on the Sequential Model Sum of Squares must have a p-value of less than 5% ($p < 5\%$). The p-value is the statistical significance or consistency of the results when repeated many times. Based on the result of p-value in the quadratic model of 0.0265 which shows that the probability of linear model error is 0.265% so that the quadratic model is suggested. The cubic model also has a p-value of less than 5% at 0.0107, but this model is not recommended.

The next model selection is based on the Lack of Fit Tests. The model that is considered appropriate is a model that is not statistically real. The model will be accepted if in this process has a P-value of more than 5% ($P > 5\%$) which shows the model is not real to the response. The results of the model selection based on the Lack of Fit Tests produce a quadratic model as a suggested model with the listed information suggested. The quadratic model has a P-value that is closer to 5% compared to the linear model and 2FI. The cubic model is not recommended by the program because the cubic model is not supported by designs that use two variables. So that the program listed the information aliased on the cubic model even though the model has a P value of 0.7003 (70.03%) or according to the requirements of $P > 5\%$.

Analysis of the final model selection is to use the Summary Statistics Model. The determination of the model in this method is based on the maximum standard deviation and $R^2$ values. The parameters used in choosing the right model are the lowest standard deviation, the highest $R^2$, the highest Adjusted $R^2$, the highest Predicted $R^2$ and the lowest PRESS. Based on the result, the model suggested is a quadratic model that has a standard deviation of 1.50. The standard deviation value is smaller than the standard deviation value of the linear model and the two-factor interaction model (2FI). While the cubic model is not recommended by the program, it is indicated by the statement aliased. The $R^2$ value of the quadratic model of 0.6875 indicates that the two independent variables i.e. the zeolite concentration and the adsorption time affect the water content loss of palm oil by 68.75%. While the remaining 31.25% is influenced by other factors. Based on the three methods in the analysis of the statistical model selection, it can be concluded that the model chosen to explain the relationship between the zeolite concentration and the adsorption time to minimize the water content loss of palm oil is the quadratic model.

Based on the analysis, a second-order polynomial equation is obtained in the form of actual variables. P-value in the form of actual variables is as follows:

\[
Y_{\text{water content loss}} = -28.57404 + 0.34787x_1 + 0.46029x_2 + 2.95074E - 003x_1x_2 0.02727x_1^2 - 1.97944E - 003x_2^2
\]

in which $x_1$ is zeolites concentration and $x_2$ is adsorption time.
Based on these mathematical equations, it can be compared with the results of the study which can be seen in Figure 1 to determine the accuracy of the model. The distribution of the actual and predicted values in Figure 1 illustrates the standard deviation of 1.50 and the $R^2$ value of 0.6875 so that it has good results even though there are some actual values that are scattered far from predictions.

**Figure 1.** Distribution of actual value distribution and predicted value of water content loss.

The graph of the contour response of water content loss can be seen in Figure 2. The contour graph is used to analyze the effect of interactions between factors on response. The outermost line on the graph shows the lowest response value and inward shows the higher response value. Figure 2b shows a three-dimensional surface graph showing that the zeolite concentration and adsorption time variables have an influence on the water content loss in the biodiesel pretreatment. Based on 3D graphics, the effect of zeolite concentration and adsorption time on water content loss form a graph like a mountain. This means that at certain conditions, water content loss indicates a peak point. Then after that, in a certain zeolite concentration and a certain adsorption time can decrease again. This decrease condition occurs due to zeolite adsorbent work that is less than the maximum or with a small amount so that it is unable to adsorb optimally.

**Figure 2.** Response to water content loss: (a) 2D; (b) 3D.

Optimization of the response to water content loss is done to determine the best treatment value in producing the optimum response value. Based on data processing, the optimum value can be seen in Table 2. Based on Table 2, it can be seen that the optimum zeolite concentration is 13.204% and the optimum adsorption time is 126.109 minutes with the optimum water content loss response is 2.745%. The desirability value at this point is 0.898. The desirability value is used to determine the accuracy of the optimal solution with a range of values from 0 to 1 where 1 indicates that the response is the perfect case while 0 indicates the response must be discarded [18]. So that the desirability value of 0.898 can indicate the accuracy of the optimum point response in this study of 89.8% as shown in Figure 3.
Table 2. Optimum points selected.

| Zeolit concentration (%) | Adsorption time (minute) | Water content loss (%) | Desirability |
|--------------------------|--------------------------|------------------------|--------------|
| 13.204                   | 126.109                  | 2.745                  | 0.898        |

The optimum model validation is used to test the accuracy of the model in describing empirical conditions. Validation is done by comparing the results of predictions and research results. The results of the validation of the optimum model conditions can be seen in Table 3. The value of actual water content loss with the zeolite concentration of 13.204% and the adsorption time of 126.109 minutes is 2.704%. The results were obtained from an average of three samples with the same treatment, where the results of the water content loss of the three samples were 2.68, 2.74, and 2.69%. Validation results can be said to be good if the predicted and actual results have an error rate of less than 5%. Whereas in this study, the error rate was 4.2% so the results of the study could be said to be valid.

Table 3. Validation result.

| Variable                  | Optimum value | Water content loss (%) |
|---------------------------|---------------|------------------------|
| Zeolit concentration (%)  | 13.204        |                        |
| Predicted                 | Actual        |                        |

4. Conclusion

The results of zeolite concentration and adsorption time modeling and optimization of the water content loss in biodiesel pretreatment are quadratic. The optimization results with response surface methodology (RSM) obtain an optimum value of 13.204% for the zeolite concentration and 126.109 minutes for the adsorption time with the optimum value of the water content loss of 2.745%. Validation carried out with three replications obtained an average water content loss of 2.704% where the results differ only 4.2% from the predicted results, so it can be concluded that the results of this study are valid.

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