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Modelling and optimization of free fatty acid reduction in bulk palm cooking oil

W Kristianingsih[1], V Liana[2], B Rohmatulloh[1], I Prakoso[3], M R Fauzy[4], B D Argo[1] and Y Hendrawan[1*]

[1]Department of Agricultural Engineering, Universitas Brawijaya, Jl. Veteran, Malang, ZIP 65145, Indonesia
[2]Department of Agroindustrial Technology, Universitas Brawijaya, Jl. Veteran, Malang, ZIP 65145, Indonesia
[3]Department of Agricultural Product Technology, Universitas Brawijaya, Jl. Veteran, Malang, ZIP 65145, Indonesia
[4]Department of Industrial Engineering, Universitas Merdeka, Jl. Terusan Raya Dieng 62-64, Malang, ZIP 65146, Indonesia

E-mail: yusuf_h@ub.ac.id

Abstract. Bulk cooking oil from palm oil processing is one of the biodiesel materials which is available in large quantities. The pre-treatment process can be done by adding 100 mesh activated zeolite adsorbent as a substitute for the esterification process to reduce free fatty acid (FFA). The purpose of this research was to model and optimize the zeolite concentration and adsorption time to reduce free fatty acids in bulk palm cooking oil. This study used a response surface method with a central composite design (CCD), resulting in 13 experimental combinations of two factorial treatments, i.e. the concentration of zeolite adsorbent and adsorption time. The zeolite concentration and the adsorption time with an upper limit of 30% and 120 minutes and a lower limit of 10% and 60 minutes had a significant effect on the FFA reduction. The best model was a quadratic model. The testing of validation data used the recommended optimum combination, i.e. the zeolite concentration of 10.59% and the adsorption time of 101.57 minutes resulting in a deviation of 5.37% between the predicted data and the actual data.

1. Introduction

Biodiesel is a type of fuel produced from processing vegetable and animal oils into a monoalkylester form through a transesterification process. Some countries have started to intensify biodiesel production because it can reduce dependence on natural fuels [1]. Palm cooking oil is a type of vegetable oil that can be used as a raw material of biodiesel with the main component of triglycerides in the form of glycerol, palmitic acid of 41.8-46.8%, stearic 4.2- 5.1%, and linoleic 9.1-11.0% [2]. The principle of transesterification is to replace the organic group R″ in an ester such as triglycerides in palm cooking oil with the organic group R′ from alcohol, such as methanol, ethanol, propanol, butanol, and amyl alcohol with the help of catalysts such as NaOH, KOH, $NaOCH_3$, and $KOCH_3$. The output of this process is new ester groups or commonly referred to as biodiesel [3]. Apart from containing triglycerides, palm cooking oil also contains free fatty acid (FFA). FFA is a saturated and long-chain free fatty acid whose amount must be controlled through the esterification process so that it does not form soap due to reacting with alkaline catalysts during the transesterification process [4].

Esterification as part of the pre-treatment process to reduce the FFA value is a reversible reaction that requires the addition of catalysts and excess reactants so that the reaction shifts to the right [5]. This method is considered to have several shortcomings because the process is slow, and the price of catalysts such as HCl, H_2SO_4, or H_3PO_4 is relatively expensive. Therefore, zeolite is used as a group of inorganic minerals which, in a certain size, can act as an adsorbent in the adsorption process. It has many pores and has a high cation exchange capacity, can be applied in a wide temperature range [6], and has been proven to be able to reduce the FFA content in cooking oil [7]. The adsorption process of zeolites is influenced by the type of adsorbent, surface area, pH, contact time, and concentration [8].

The reduction in FFA values in cooking oil is influenced by two independent variables i.e. zeolite concentration and adsorption time [9]. The use of zeolite at the appropriate concentration is necessary because saturation will arise at a certain point of the adsorbent used. The adsorption time factor is also considered to be influential to the condition that the adsorption of FFA by zeolite is a type of physical adsorption that is reversible so that it allows desorption or re-release adsorbate molecules at the same temperature [10].

In order to obtain the best reduction in FFA values, based on the right combination of independent variables, the zeolite concentration factor (X_1) and adsorption time (X_2) can be optimized through statistical and mathematical data analysis processes using the response surface method (RSM) [11]. The advantage of RSM can explain the relationship of quantitative independent variables to the response (order II model) and can explain the relationship of variables to responses visually through contour plots and surface plots [12]. Many researchers have conducted a study on the optimization of FFA reduction using RSM with a central composite design (CCD) [13][14]. The CCD can be a combination of a 2^k (order I) factorial design added with 2^k axis points (α) and n_0 at the center point [15]. The advantage of CCD can describe a stationary point so that it can be seen whether the optimization of data is maximum, minimum, or at a saddle point [16]. The purpose of this study was to model and optimize the zeolite concentration and adsorption time to reduce the FFA value of bulk palm cooking oil.

2. Material and methods

2.1. Tools and materials

The research was conducted at the Basic Chemistry Laboratory, Faculty of Agricultural Technology, Universitas Brawijaya. The tools used in this study were: blender (Philips HR type 2116 / AI 220-240V / 350W ser. 1322) to shrink the zeolite size; 100 mesh filter to uniform zeolite size; oven (Medcenter-Ecocell 55 / 230V / 1290W) for drying zeolites before and after activation; pH meter (Crison with No. Series 210325) for measuring zeolite pH during the washing process; analytical balance (Mettler PM460) for weighing materials; hot plate stirrer as a heat source for the adsorption process; mercury thermometer to measure the temperature of the sample during the adsorption process. The materials in this study included: 100 mesh activated natural zeolite as an adsorbent; distilled water as material for zeolite pre-treatment and dilution of H_3PO_4 and NaOH; 2M H_3PO_4, as a material for the activation of natural zeolites; bulk palm cooking oil as the main research material; 95% ethanol as test material for FFA content; PP indicators as test materials for FFA content; and 0.1 N NaOH as a material for the titration process.

2.2. Experimental setup

Preliminary research was carried out using several variations of zeolite concentration and adsorption time. The result showed an optimal FFA reduction was at a zeolite concentration ratio of 1:5 to 50 g and an adsorption time of 90 minutes. Based on these results, a preliminary study was carried out with a 1:5 concentration of zeolite concentration against 50 g of bulk palm cooking oil mass (w/w) with an adsorption time of 90 minutes to ensure that there was no greater decrease in the FFA value. It can be concluded that the treatment with a zeolite concentration ratio of 1:5 and an adsorption time of 90 minutes was the initial optimal point.

2.3. Analysis

The study was designed using the RSM-CCD with data processing by Design Expert 10.0.8. This study was influenced by two independent factors and 1 response i.e. FFA reduction (%). The first factor was the zeolite concentration (% oil), and the second factor was the adsorption time (minutes). Based on the results of preliminary research, the optimal FFA reduction was the treatment of zeolite concentration of 1:5 (20%) and the adsorption time of 90 minutes, so the determination of the zeolite concentration factor had a lower limit of 10% (-1 level) and an upper limit of 30% (+1 level). Meanwhile, the adsorption time had a lower limit of 60 minutes (-1 level) and an upper limit of 120 minutes (+1 level). After being combined using the Design Expert 10.0.8 application, 13 experimental designs were produced. The selection of the best model can be determined based on several criteria i.e. the Sequential Model Sum of Squares, the Lack of Fit test, and the Model Summary Statistics. The selection of the best statistical model based on the Model Summary Statistics was one method of testing by referring to the standard deviation value and the value of R squared (R^2). The best model was determined by the lowest standard deviation value, the highest R^2 value, and several other components such as the Adjusted R-square, Predicted R-Square, and the PREES value. The recommended model was then analyzed using analysis of variance (ANOVA) to determine the relationship between the zeolite concentration and the adsorption time to the response, i.e. the FFA reduction.

The adsorption process was carried out by preparing 50 g of oil or 53.6 mL and pouring it into a 500 mL beaker glass. Furthermore, zeolite was added according to the experimental design produced by RSM. The oil used in this research was bulk palm cooking oil, which had an initial FFA level between 0.15% -0.3%. Then the sample was heated and stirred with a hot plate magnetic stirrer and was kept constant at 90 °C with the aim that the zeolite adsorbent can work evenly in all parts of the oil sample and can reduce the viscosity of the oil so that adsorption runs optimally due to freer molecular movement. The adsorption process was carried out over a period of time according to the RSM design. Testing the FFA content and decreasing the FFA value was carried out by measuring 10.7 mL of oil and put in a 250 mL Erlenmeyer glass, then adding 25 mL of 95% ethanol and heated at 40 °C and stirring until the solution was homogeneous. In the next step, 2 mL of PP indicator was added and titrated with 0.1 N NaOH solution until a pink color appeared and did not disappear for 30 seconds. The FFA reduction is obtained from reducing the initial FFA content of the oil sample before adsorption by the FFA content of the oil after adsorption.

3. Results and discussion

3.1. RSM modelling results

The results of the experimental study are presented in Table 1. The initial FFA value of bulk palm cooking oil without adsorption treatment was 0.138%. The treatment of zeolite concentration and adsorption time in several combinations showed a negative response value. This means that the sample did not decrease the FFA value. This condition can be explained because there were circumstances where the uncontrolled water content in the sample can act as a triglyceride separator so that it broke down into FFA and glycerol. The optimum point area test designed by CCD was carried out at a zeolite concentration of 20% and an adsorption time of 90 minutes, with 5 replications resulting in the FFA reduction between 0.022 to 0.033%. So based on the overall data generated, the largest FFA reduction was in the combination of zeolite concentration and adsorption time of 20% and 90 minutes which resulted in the FFA reduction of 0.033%. The smallest FFA reduction was in the combination of zeolite concentration and adsorption time of 34% and 90 minutes with the FFA reduction of -0.680%. In general, the results of this study prove that the use of zeolite at a certain amount can be used as an adsorbent to reduce the FFA in the biodiesel pre-treatment process.

The results showed that the best-recommended model was the quadratic model with a P-value of 0.0249 and there was suggested information in Table 2. The p-value which was more than 5% for the linear model and the 2FI model respectively, were 0.1317 and 0.4141 so that the two models were considered less precise than the quadratic model. The cubic model showed a small P-value of 0.0036, however, it was not recommended because there was Aliased information in the right column. The results in Table 3 showed that the best model suggested was the quadratic model. The results in Table 4 showed that the best model suggested was the quadratic model.

Table 1. Research results on Design Expert 10.0.8.

	Actual variable		Coded variable		Response variable
Std	Zeolite concentration (% oil)	Adsorption time (minutes)	X_1	X_2	response 1: FFA reduction (%)
1	10	60	-1.00	-1.00	-0.089
2	30	60	1.00	-1.00	-0.003
3	10	120	-1.00	1.00	-0.011
4	30	120	1.00	1.00	-0.234
5	5.85786	90	-1.41	0.00	0.011
6	34.1421	90	1.41	0.00	-0.680
7	20	47.5736	0.00	-1.41	0.020
8	20	132.426	0.00	1.41	0.019
9	20	90	0.00	0.00	0.022
10	20	90	0.00	0.00	0.033
11	20	90	0.00	0.00	0.022
12	20	90	0.00	0.00	0.025
13	20	90	0.00	0.00	0.022

Table 2. Model selection by Sequential Model Sum of Squares.

Source	Sum of Squares	df	Mean Square	F Value	p-value prob > F	
Mean vs Total	0.044	1	0.044			Suggested
Linear vs Mean	0.13	2	0.064	2.50	0.1317	
2FI vs Linear	0.019	1	0.019	0.73	0.4141	
Quadratic vs 2FI	**0.15**	**2**	**0.077**	**6.55**	**0.0249**	**Suggested**
Cubic vs Quadratic	0.074	2	0.037	21.18	0.0036	Aliased
Residual	8.709E-003	5	1.742E-003			
Total	0.43	13	0.033			

Table 3. Model selection using Lack of Fit Tests.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Linear	0.26	6	0.043	2257.26	< 0.0001	
2FI	0.24	5	0.047	2504.64	< 0.0001	
Quadratic	0.082	3	0.027	1452.26	< 0.0001	Suggested
Cubic	8.633E-003	1	8.633E-003	456.41	< 0.0001	Aliased
Pure Error	7.566E-005	4	1.892E-005			

3.2. ANOVA analysis

The ANOVA results in this study are presented in Table 5. Based on the ANOVA results, the model was significant because it had an F value of 5.12 and a P-value of 0.0270, which means that there was a 2.7% chance for the F value to occur noise. The regression model was considered to have a significant effect on the response, i.e. the FFA reduction, because the zeolite concentration factor had met the criteria i.e. having a P-value of 0.0137 where the value was less than 5%. Although the P-value for the adsorption time was 0.6648 which was more than 5%, the P-value on the Lack of Fit line had a value of <0.0001 or less than 5% (P-value <5%) which indicated that this value was significant. This showed that the quadratic was the most suitable model. Based on the analysis using Design Expert 10.0.8, it was found that the polynomial equation of the second-order model was in coded and actual form. The RSM coded equation as follows:

$$Y = 0.022 - 0.13\,{}^{*}X_1 - 0.017\,{}^{*}X_2 - 0.069\,{}^{*}X_1X_2 - 0.15\,{}^{*}X_1^2 + 0.014\,{}^{*}X_2^2 \quad (1)$$

The RSM actual equation as follows:

$$Y = (-0.5469) + (0.066411X_1) + (1.25880 \times 10^{-3}X_2) - (2.31544 \times 10^{-4}X_1X_2) - (1.45271 \times 10^{-3}{X_1}^2) + (1.55199 \times 10^{-5}{X_2}^2) \quad (2)$$

Where Y was the response to the FFA reduction, X_1 was the zeolite concentration and X_2 was the adsorption time.

Table 4. Model selection using Model Summary Statistics.

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.16	0.3333	0.2000	-0.3836	0.53	
2FI	0.16	0.3835	0.1781	-0.6080	0.62	
Quadratic	0.11	0.7854	0.6321	-0.5249	0.59	Suggested
Cubic	0.042	0.9773	0.9456	-0.4377	0.55	Aliased

Table 5. The Results of ANOVA.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.30	5	0.060	5.12	0.0270	*significant*
A-zeolite concentration	0.13	1	0.13	10.67	0.0137	
B-adsorption time	**2.410E-003**	**1**	**2.410E-003**	**0.20**	**0.6648**	
AB	0.019	1	0.019	1.64	0.2414	
A^2	0.15	1	0.15	12.46	0.0096	
B^2	**1.357E-003**	**1**	**1.357E-003**	**0.12**	**0.7443**	
Residual	0.082	7	0.012			
Lack of Fit	0.082	3	0.027	1452.26	< 0.0001	*significant*
Pure Error	7.566E-005	4	1.892E-005			
Cor Total	0.38	12				
Std. Dev.	0.11		R-Squared	0.7854		
Mean	-0.058		Adj R-Squared	0.6321		
C.V. %	186.09		Pred R-Squared	-0.5249		
PRESS	0.59		Adeq Precision	7.055		

From the comparison results of the FFA reduction between actual and predicted values, the range was between 0-0.167, so the difference between actual and predicted values was not too far away and were acceptable. The accuracy of the model can be seen from the small difference between the actual value and the predicted value of the model. Figure 1 showed the distribution of the actual and the predicted value, with a standard deviation value of 0.11 and an R^2 value of 0.78 which was a fairly good result.

Figure 2a was a cross-sectional image of a three-dimensional curve that can show the effect of the interaction between factors in the response. Based on the contour plot, the zeolite concentration and the adsorption time factor had a significant effect on the FFA reduction which was indicated by a bright red area. The outermost line on the graph for areas with greater zeolite concentration and adsorption time showed a red color that tends to fade and change to yellow and even green, indicating that the response value had decreased even though it was not too significant. The response given was also presented in the form of a 3D surface as shown in Figure 2b. The higher the value of the combination between the zeolite concentration and the adsorption time factor, the lower the FFA reduction due to the catalytic conversion of FFA by zeolites via esterification and transesterification at a longer time [17].

3.3. Model validation

Based on the preliminary research, the lower limits for zeolite concentration and adsorption time were 10% and 60 minutes, respectively, and the upper limits were 30% and 120 minutes, respectively. Meanwhile, the desired parameter for the FFA reduction was maximizing or the result of the largest FFA reduction in response with a lower limit of -0.612% and an upper limit of 0.30%. Based on these criteria, Table 6 shows the optimal solution. The optimum point with the best response results was obtained at a combination of zeolite concentration of 10.59% and the adsorption time of 101.6 minutes which resulted in the FFA reduction of 0.032%. This combination had a desirability value of 1.00 (as shown in Figure 3) which means that the response was in perfect condition [18]. In the process of testing the validation data, by comparing the actual and predicted results, an error rate of 5.37% was obtained.

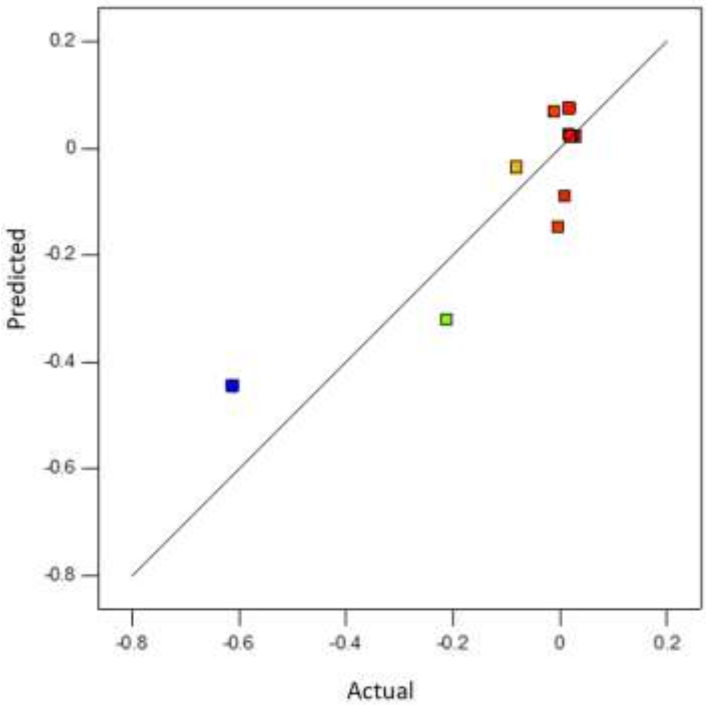
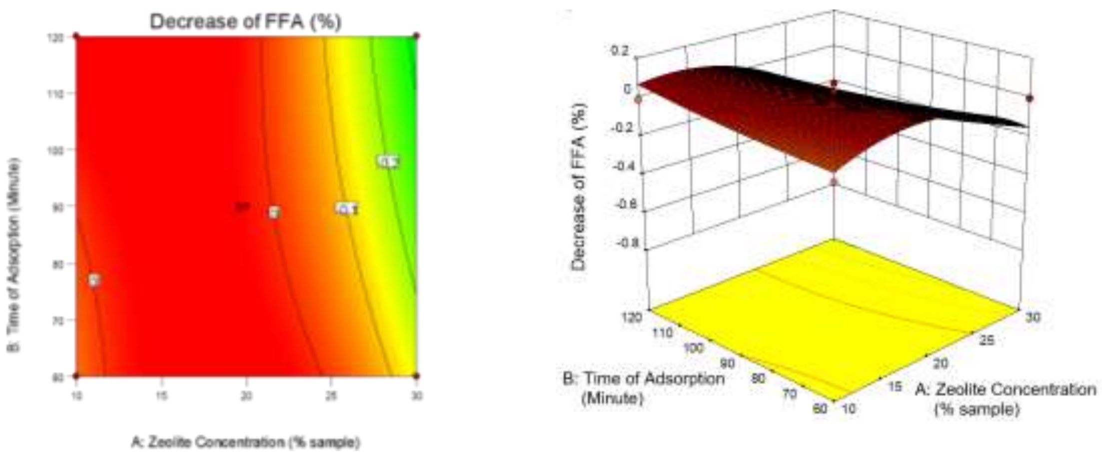


Figure 1. Comparison of actual and predicted value.

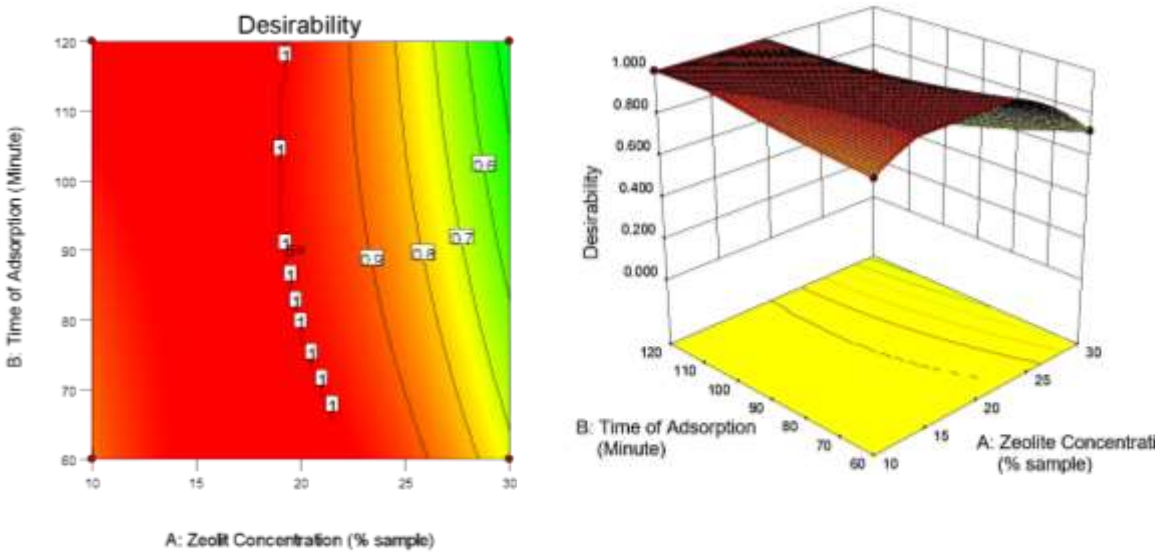


(a) (b)

Figure 2. Response to the decrease of FFA: (a) 2D; (b) 3D.

Table 6. Optimal results using RSM.

Zeolite concentration (% oil)	Adsorption time (minutes)	FFA reduction (%)	Desirability	
10.594	101.571	0.032	1.000	*Selected*



(a) (b)

Figure 3. Desirability: (a) 2D; (b) 3D.

4. Conclusions

Bulk cooking oil from palm oil processing is pre-treated with zeolites to reduce free fatty acid (FFA). The increasing combination of zeolite concentration and the adsorption time lowered the FFA reduction due to the catalytic conversion of FFA by zeolites. The best model of the FFA reduction using RSM was a quadratic model with a desirability value of 1.00 which means that the response was in perfect condition. The optimum point of zeolite concentration was 10.59% with adsorption time of 101.57

minutes, which resulted in FFA reduction of 0.032%. In the process of testing the validation data, by comparing the actual and predicted results, an error rate of 5.37% was obtained.

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