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Optimization of Reducing Waste Cooking Oil's FFA Content as Biodiesel Feedstock

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ABSTRACT

Waste cooking oil has high Free Fatty Acid (FFA). It affected on decreasing a biodiesel production. FFA reduction is one of important processes in biodiesel production from waste cooking oil. Thus, this study aimed to examine the optimum condition in FFA reduction. The process is assisted by using ultrasonic irradiation on acid esterification. Variables of the process are acid concentration, molar ratio of methanol and oil, and irradiation time. Meanwhile temperature irradiation on 45°C is a control variable. Process optimization is conducted by Response Surface Methodology (RSM) with Central Composite Design (CCD). The optimum conditions of response were 7.22:1 (methanol to oil molar ratio), 0.92% wt H_2SO_4, 26.04 minutes (irradiation time), and 45°C (irradiation temperature). Ultrasonic system reduced FFA significantly compared to conventional method.

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1. INTRODUCTION

Biodiesel is considered as an alternative fuel to decrease the dependence on petroleum fuel. It is from renewable resources such as edible oils, non-edible oils, algae, fats, and waste cooking oil. Waste cooking oil (WCO) is waste based oil. It is a non-edible oil with large capacity. It has a potential as biodiesel feedstock [1]. However, it has high free fatty acid (FFA) that affect to biodiesel yield. FFA can be reduced by acid esterification. Esterification is the reaction of two immiscible phases. The less dense phase dissolves the catalyst in the alcohol, while the other phase contains oil. The reaction between the two immiscible phases occurs in the area of the interface between the liquids. Interface area between phases should be increased by vigorous mixing such as ultrasonic irradiation in order to increase rate of reactions [2]. It emulsify immiscible liquids.

Thus, this study is applied ultrasonic irradiation. It produces bubble cavitation around boundary phase between the alcohol phase and the oil. Emulsification is generated during rupture of cavitation bubbles that break boundary phase. Ultrasound assists penetration one liquid to another liquid [3]. Temperature increases locally at boundary phase due to cavitation, thereby transesterification reaction enhances significantly [4-5].

Response Surface Method (RSM) is a powerfull statistical method that has been carried out in many studies [6]. Multiple regression and correlation analysis are applied as tools to examine the influence of two or more independent factors toward dependent variables. In addition, optimization design of some operation conditions in biodiesel production and biomass technology conducted by the Central Composite Design (CCD). The main advantage is to reduce required experimental numbers to provide enough information in obtaining significant findings statistically. It has been successfully carried out to optimize the production of biodiesel in oil feedstocks, including Madhuca indica, Jatropha curcas oil, and animal fats [7-10]. In the recent study, esterification based acid is used to reduce high free fatty acid (FFA) of waste cooking oil. Optimization of process variable is less than 1% FFA by using RSM in design of experiments.

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2. METHODS

Waste cooking oil was purchased from several fried chicken restaurants in Padang, West Sumatera, Indonesia. Methanol and H_2SO_4 were supplied from Systerm. Characteristics of WCO are reported in Table 1.

Table 1: Characteristics of waste cooking oil

Characteristics	Values
% FFA	14.2
Acid Value, mg KOH/g oil	28.258
Moisture content, % w/w	2.31
Iodine Value, mg/g oil	102.85
Saponification Value, mg KOH/g oil	192.52
Viscosity, cSt	46.85
Density at 20^{o}C, g/cm^3	0.9114

2.1 Experimental design

This study employed RSM with Central Composite Design (CCD). Three process variables are set as independent variables. Those are concentration of sulfuric acid (% H_2SO_4) (C), molar ratio of methanol to oil (M), and irradiation time (t). Dependent variable is free fatty acid (%FFA). A five-level-three-factors CCD was carried out in this study for 20 experiments (2k + 2k + 6). k is the number of independent variables. The level of uncoded and coded (actual) of independent variables are described in Table 2.

Table 2: Independent variable and levels used for CCD in acid transesterification process

Variable	Symbol	Level[a]				
		- 1.68 (-α)	**-1**	**0**	**1**	**1.68 (α)**
Methanol to oil molar ratio	M	2.30 : 1	4 : 1	6.50 : 1	9 : 1	10.70 : 1
% H_2SO_4 (%w)	C	0.16	0.5	1.0	1.5	1.84
Irradiation Time (minute)	t	3.20	10	20	30	36.80

aTransformation of variable levels from coded (X) to uncoded could be obtained as :

Mu = 6.50+2.50X, Cu = 1+0.5X, tu = 20+10X

2.2 Acid esterification process

Acid esterification was carried out using equipment setup as shown in Figure 1. The ultrasonic generator was a Trans-O-Sonic from Shanti Industrial Estate, India. Its frequency is 30 ± 3 KHz and power was 250 Watt. Approximately, 12 g of oil was poured in the round bottom flask. It was heated at 45^{o}C and irradiated by ultrasonic. Subsequently, the certain amounts of methanol and sulfuric acid were poured to the oil. Temperature was kept constant during esterification process. Heating and ultrasonic irradiation were stopped after irradiation has reached the irradiation time. The flask was immersed in cold water immediately for stopping the reaction. The mixture was stand until separated into two layers. The bottom layer was drained whereas the upper layer was washed by hot water for removing the impurities then dried for further analysis (% FFA).

Replications were conducted twice for all experimental runs. The value of alpha (α) was fixed 1.68. The central point (zero level) for each independent variable was 6.50 : 1 for molar ratio of methanol and oil, 1% H_2SO_4 of % catalyst, and 20 minutes for irradiation time. Experiments are conducted in random order.

2.3 FFA examining

FFA content was examined as percentage of oleic acid. Potassium hydroxide (KOH) was used as standard alkali solution. This quantitative analysis was examined based on AOAC (Association of Official Agricultural Chemists) Official Method Cd 3a-63.

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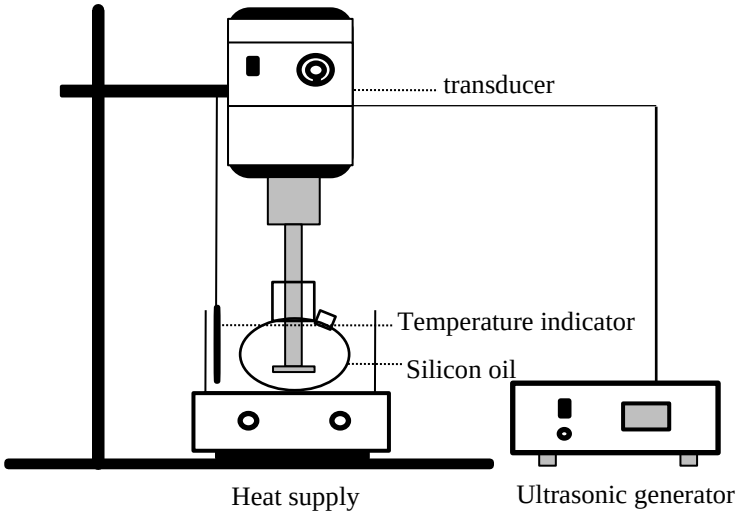

Figure 1: A schematic experimental of acid esterification

2.4 Analysis of statistics

Second-order polynomial was applied in analysis as shown in Equation 1:

$$y = \beta_o + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i>j}^{3} \sum_{j}^{3} \beta_{ij} x_i x_j + e \quad (1)$$

Where y is the response (percentage of free fatty acid, % FFA); βo is intercept, βi is linear constant coefficients, βii is quadratic constant coefficients, and βij is interaction constant coefficients. xi and xj are the uncoded independent variables; e is the error. Design Expert 6.0.10 (STAT-EASE Inc) is applied to examine analysis of regression and analysis of variance (ANOVA). Validation of equation is conducted by confirmatory experiments using combinations of independent variables. It is within the experimental area but not part of the original experimental design [7]. The coefficient of determination (R^2) is used to evaluate the quality of the model fit, and the response surfaces are drawn using the fitted quadratic polynomial equation obtained through regression analysis.

3. RESULTS AND DISCUSSION

In this section, it is explained the results of research and the comprehensive discussion. Results were presented in figures and tables [2], [5].

3.1 Model fitting and anova

Table 3 shows the experimental and predicted values of the free fatty acid response percentage obtained at the design point. All variables are displayed in coded and non-coded form.

Table 3: Central composite design arrangement and response for acid catalyzed esterification

No.	M		C		t		%FFA	
	coded	Actual	coded	actual	coded	actual	Experimental	Predicted
1	-1	4:1	-1	0.5	-1	10	6.21	6.12
2	1	9:1	-1	0.5	-1	10	2.02	2.20
3	-1	4:1	1	1.5	-1	10	4.45	4.70
4	1	9:1	1	1.5	-1	10	4.01	3.98
5	-1	4:1	-1	0.5	1	30	3.32	3.32
6	1	9:1	-1	0.5	1	30	0.41	0.12
7	-1	4:1	1	1.5	1	30	1.31	1/10

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No.	M		C		t		%FFA	
	coded	Actual	coded	actual	coded	actual	Experimental	Predicted
8	1	9:1	1	1.5	1	30	1.05	1.10
9	-1.68	2.3:1	0	1.0	0	20	4.21	4.23
10	+1.68	10.7:1	0	1.0	0	20	0.89	0.94
11	0	6.5:1	-1.68	0.16	0	20	2.10	2.21
12	0	6.5:1	+1.68	1.84	0	20	1.88	1.84
13	0	6.5:1	0	1.0	-1.68	3.20	6.20	5.99
14	0	6.5:1	0	1.0	+1.68	36.80	0.94	1.22
15	0	6.5:1	0	1.0	0	20	0.97	1.26
16	0	6.5:1	0	1.0	0	20	1.23	1.26
17	0	6.5:1	0	1.0	0	20	1.42	1.26
18	0	6.5:1	0	1.0	0	20	1.23	1.26
19	0	6.5:1	0	1.0	0	20	1.32	1.26
20	0	6.5:1	0	1.0	0	20	1.41	1.26

Quadratic polynomial model of FFA are predicted by applying Least Square technique and the Multiple Regression Coefficients of linear and quadratic terms of M, C and T shown in Table 4

Table 4: Regression coefficients of predicted quadratic polynomial model for acid catalyzed esterification

Term	Regression coefficients
Intercept	
β_o	1.26
Linear	
β_1	-0.98
β_2	-0.11
β_3	-1.42
Quadratic	
β_{11}	0.47
β_{22}	0.27
β_{33}	0.83
Interaction	
β_{12}	0.80
β_{13}	0.18
β_{23}	-0.20

Data generate a quadratic polynomial equation. Predicted value of % FFA as shown below (in terms of the code factors):

$$y = 1.26 - 0.98M - 0.11C - 1.42t + 0.47M^2 + 0.27C^2 + 0.83t^2 + 0.80MC + 0.18Mt - 0.20Ct \quad (2)$$

Where y is the response of %FFA, while M is actual values of methanol to oil molar ratio, C is % H_2SO_4 as catalyst and t is irradiation time. Analysis of the model statistically was carried out to examine adequacy of the empirical model and ANOVA. Results are summarized in Table 5.

Table 5: Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degrees of freedom	Mean squares	F-value	P-value
Model	59.04	9	6.56	128.75	<0.0001
Residual	0.51	10	0.051		
Lack of fit	0.37	5	0.074	2.70	0.1494

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Source	Sum of squares	Degrees of freedom	Mean squares	F-value	P-value
Pure error	0.14	5	0.028		
Cor total	59.55	19			

CV = 0.97, R^2 = 0.9914, Adj.R^2 = 0.9837, Predicted R^2 = 0.9452, Adeq Precision = 37.653

The model F value of 128.75 indicates that the model is valid, and the p value of the model is less than 0.0001, which indicates that the model term is very important in predicting the response value and inferring the applicability of the model. The lack of fit is the weighted sum of the squared deviations between the average response of each parameter level and the corresponding fit. The p-value for lack of fit is 0.1494, indicating that it is not significant relative to pure error. The inconspicuous fit is not good. The fitted F value is 2.70, which means that when the model is fitted to the observed experimental data, the possibility of such a large underfitting due to noise is 14.94%. CV of the model is 0.97 that closer to unity. It indicated reliability of fitted model is high. The quality of the modelfit was examined by the coefficient of determination (R^2). The R^2 value is between 0 and 1. More closer to 1 indicated reliable model. The study obtained R2 0.9914. It shows that 99.14% of the experimental data is compatible with model. The adjusted determination coefficient (adjusted R^2) value is 0.9837, which is close to R^2. It shows the experimental has strong correlation to predicted values and explains any changes in the response. Normality plot of data between student residuals and residual are shown in Figure 2.

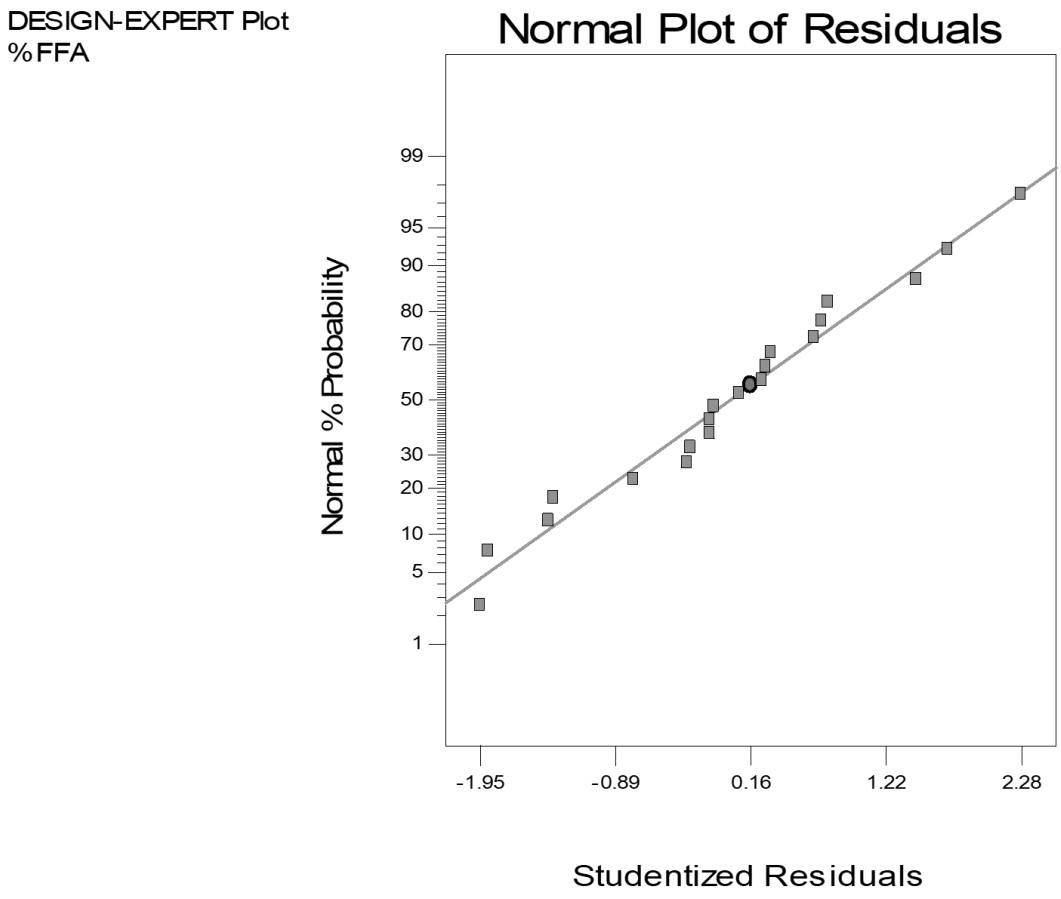

Figure 2: Normal probability plot of residuals

It shows that there is a characteristic dispersion of constant variables in the data. The model adequately explains the experimental range studied.

3.2 Interaction of parameters to FFA

Figure 3 a-c show response surface between variables for different fixed parameters.

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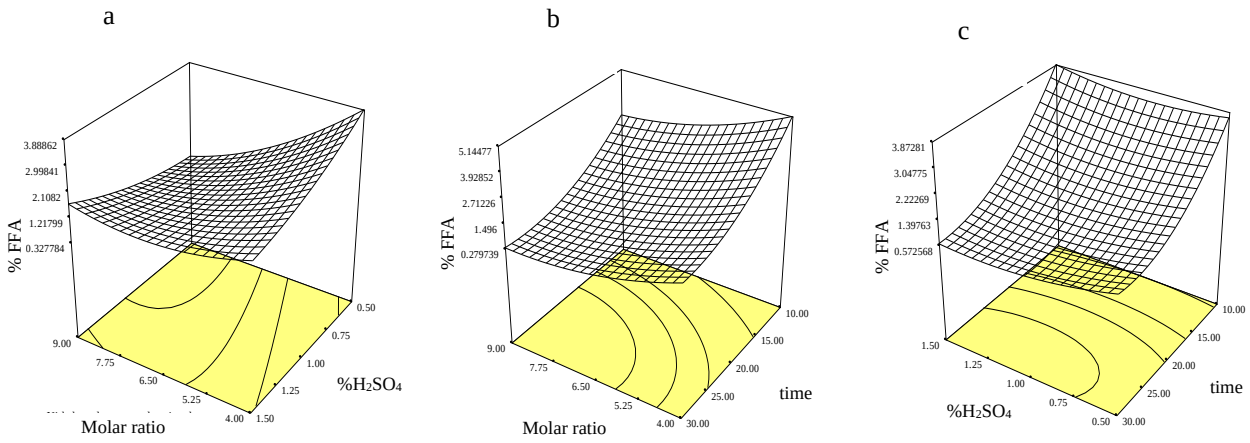


Figure 3 a-c Response surface between variables for different fixed parameters

Figure 3a shows the effect of $\%H_2SO_4$ and molar ratio of methanol and oil at 20 minutes irradiation time and 45ºC temperature. Percentage of H_2SO_4 has more significant effect on reducing FFA compared to methanol and oil ratio. Interaction between $\%H_2SO_4$ and molar ratio of methanol and oil has positive effect and significant on reducing FFA content. FFA content decreases with increasing of $\%H_2SO_4$ and molar ratio of methanol and oil. However, in achieving FFA content less than 1%, should applied less than 1.18% H_2SO_4 and more than 7.23:1 molar ratio of methanol. Figure 3b represents the effect of irradiation time at $1\%H_2SO_4$ and molar ratio of methanol and oil at 45ºC of temperature. Irradiation time has more significant effect on reducing FFA compared to molar ratio of methanol and oil. According to plot, FFA content decreases with the increasing molar ratio of methanol and oil. Whereas Figure 3c represents the effect of $\%H_2SO_4$ and irradiation time. In interaction between $\%H_2SO_4$ and irradiation time, irradiation time has more significant effect on reducing the FFA content compared to $\%H_2SO_4$.

3.3 Process optimization

Software design expert 6.0.10 is applied to examine process optimization by solving the regression equation (Equation 1). The model is used to examine the process variable with the smallest FFA content. The optimized result at 45ºC is that molar ratio of methanol and oil is 7.22:1, 0.92 wt% H_2SO_4 and 26.04 minutes of irradiation time. The model predicts that the lowest FFA content obtainable under these optimal conditions is 0.5%.

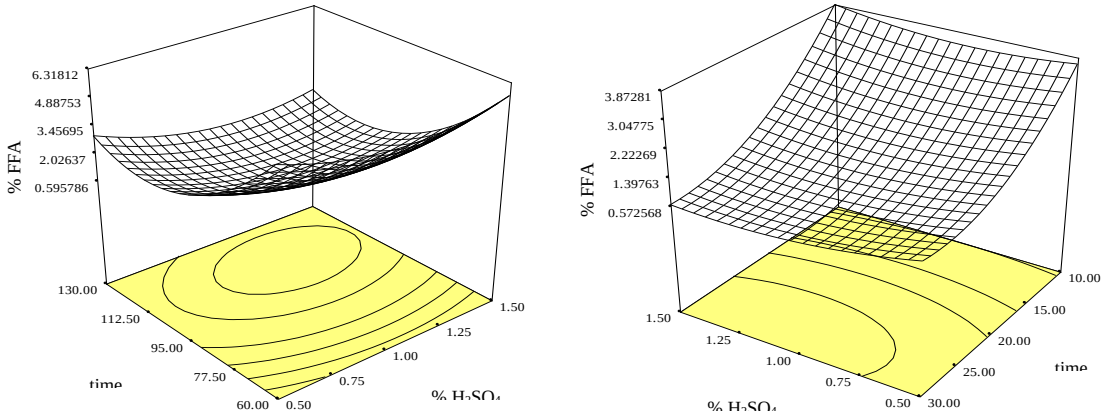
3.4 Verification of predictive model

Optimum response value was tested to verify model predicted value. It has been examined to be the optimum response through the RSM optimization method, and is also used to verify the experiment and use the model equation to predict the response value. Table 6 shows the predicted and experimental response values under the best conditions.

Table 6: Verification experimental at optimum condition

Methanol to oil molar ratio	% H_2SO_4 (%w/w)	Irradiation time (min)	Reaction temperature (ºC)	% FFA experimental	% FFA predicted
7.22	0.92	26.04		0.61	0.50

The experimental value of the FFA content is 0.61%. The experimental value is closer to the predicted value of the model. The results show the effectiveness of the RSM model, which is sufficient to reduce FFA content for esterification.



Conventional ultrasonic

Figure 4: Comparison between conventional method and ultrasonic

Figure 4 shows that catalyst performance was more effective with ultrasonic irradiation compared to conventional method. Employing equal amount of methanol and oil (6.50:1) in achieving 1% FFA, acid esterification with ultrasonic irradiation need 0.63% H_2SO_4 and 27.54 minutes, whereas by conventional method need 0.81% H_2SO_4 and 108.40 minutes. It indicates that ultrasonic irradiation reduce catalyst utilization around 21.69% and 74.59% of reaction time. Ultrasonic irradiation reduced reaction time because ultrasonic generated cavitation and increased mass transfer. Ultrasonic cavitation provided the necessary activation energy in acid esterification. Employing equal %H_2SO_4 around 1%, by ultrasonic irradiation need 5.61:1 molar ratio of methanol and oil whereas by conventional method need 5.82:1. It indicated that ultrasonic reduced methanol to oil molar ratio around 3.61%.

4. CONCLUSION

In summary, the Response Surface Methodology (RSM) with Central Composite Design (CCD) is successfully conducted to the model to optimize the independent variables for acid esterification using ultrasonic irradiation. Ultrasonic irradiation is an effective method to reduce FFA content and save time. The effect of irradiation time was more significant compared to % H2SO4 and molar ratio of methanol and oil whereas %H_2SO_4 was more significant compared to methanol to oil molar ratio in reducing FFA content by acid esterification process. RSM generated reliable model in predicting the FFA content precisely. Further, it generated the optimum value for independent parameter. Those were molar ratio of methanol and oil of 7.22:1, H_2SO_4 0.92%, and irradiation time for 26.04 minutes. Under these conditions, the FFA content can be obtained less than 1%.

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NOMENCLATURE

α	Central point
C	Concentration of catalyst
βo	Intercept
βi	Linear constant coefficients
βii	Quadratic constant coefficients
βij	Interaction constant coefficients
X	Uncoded independent variables
R^2	Coefficient of determination
K	The number of independent variables
M	Molar ratio of methanol to oil
T	Irradiation time
Y	The response (percentage of free fatty acid, % FFA

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