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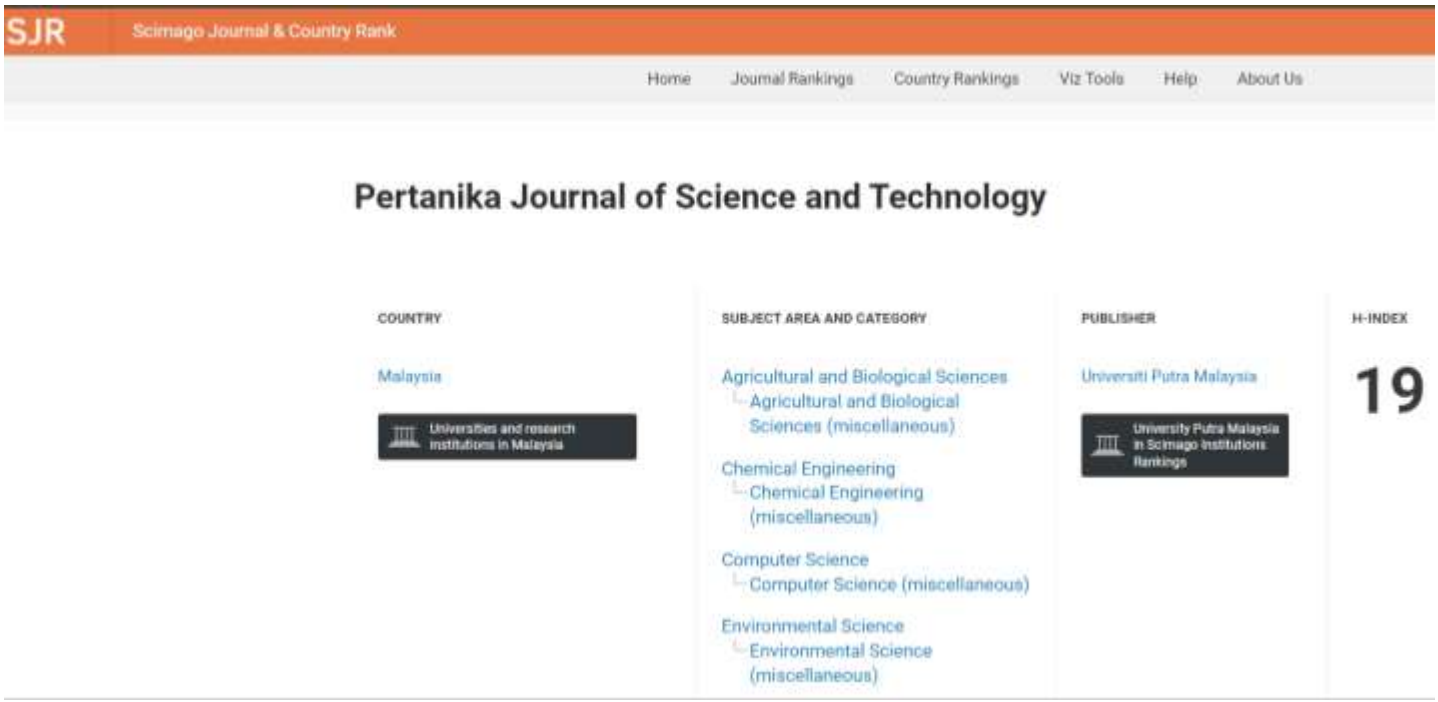

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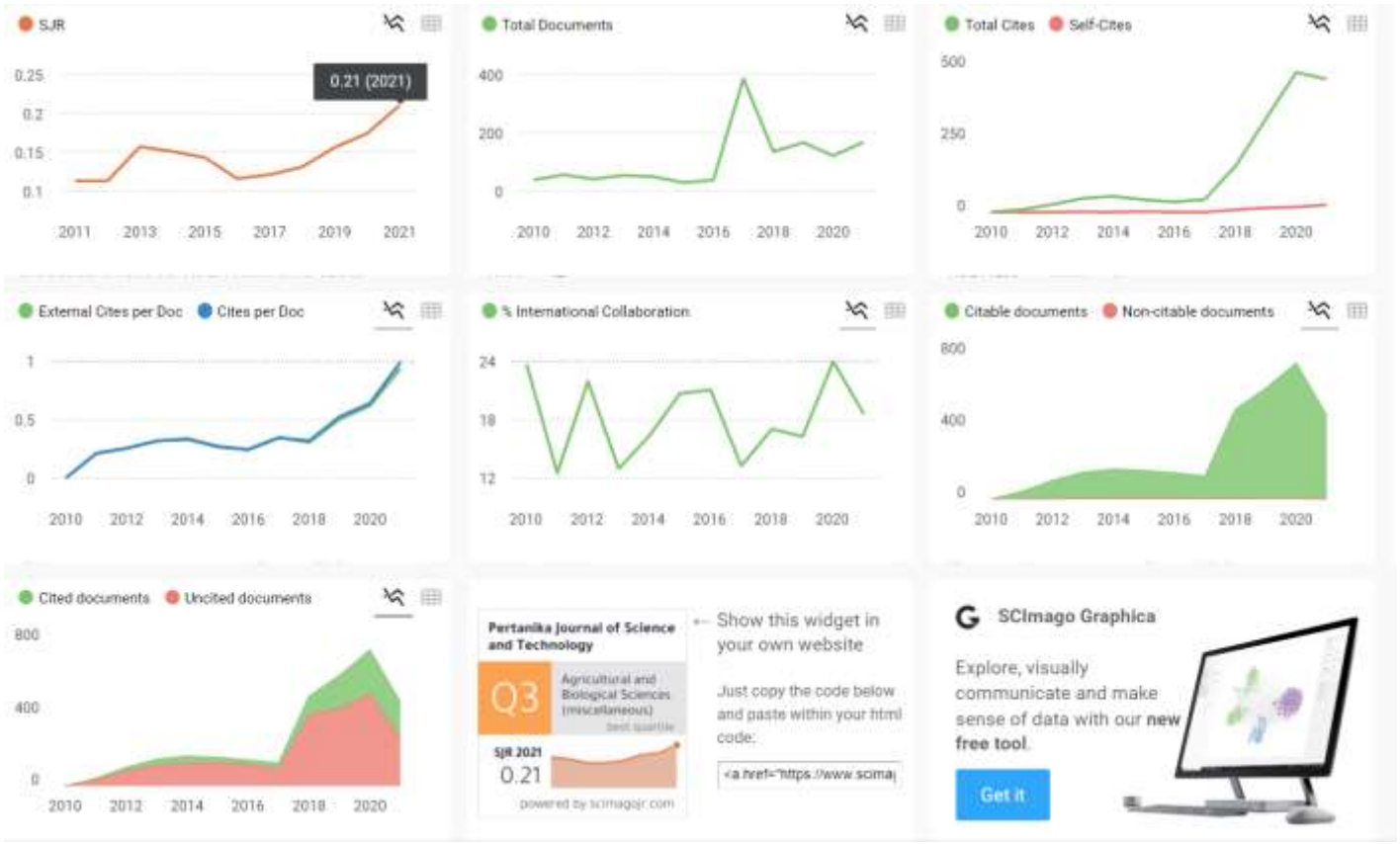

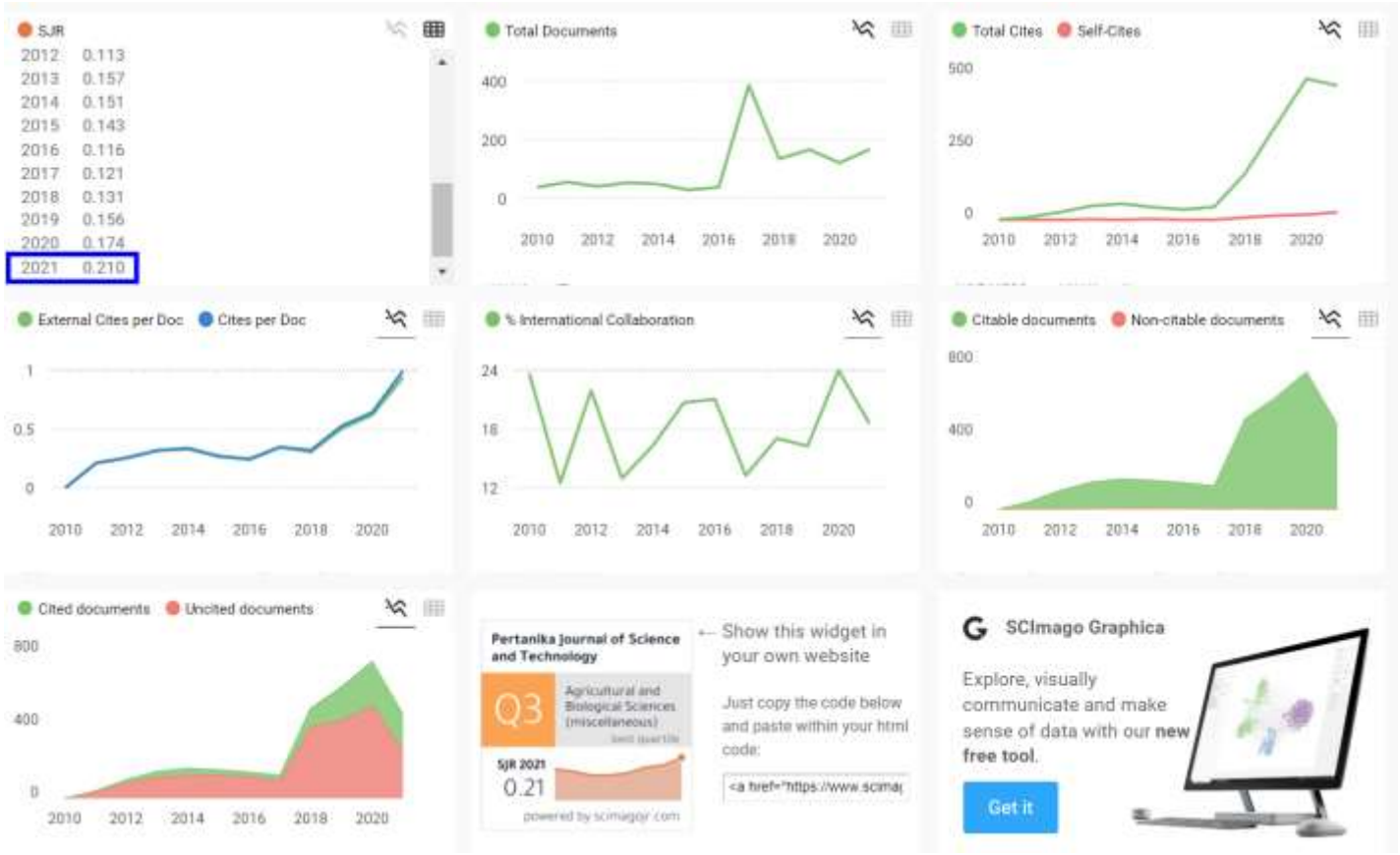

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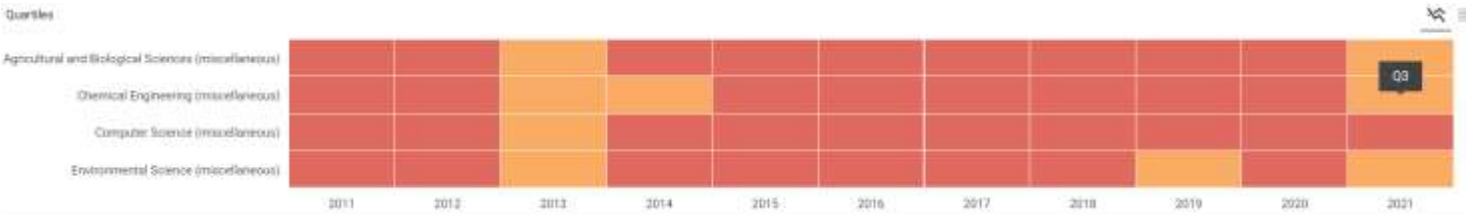

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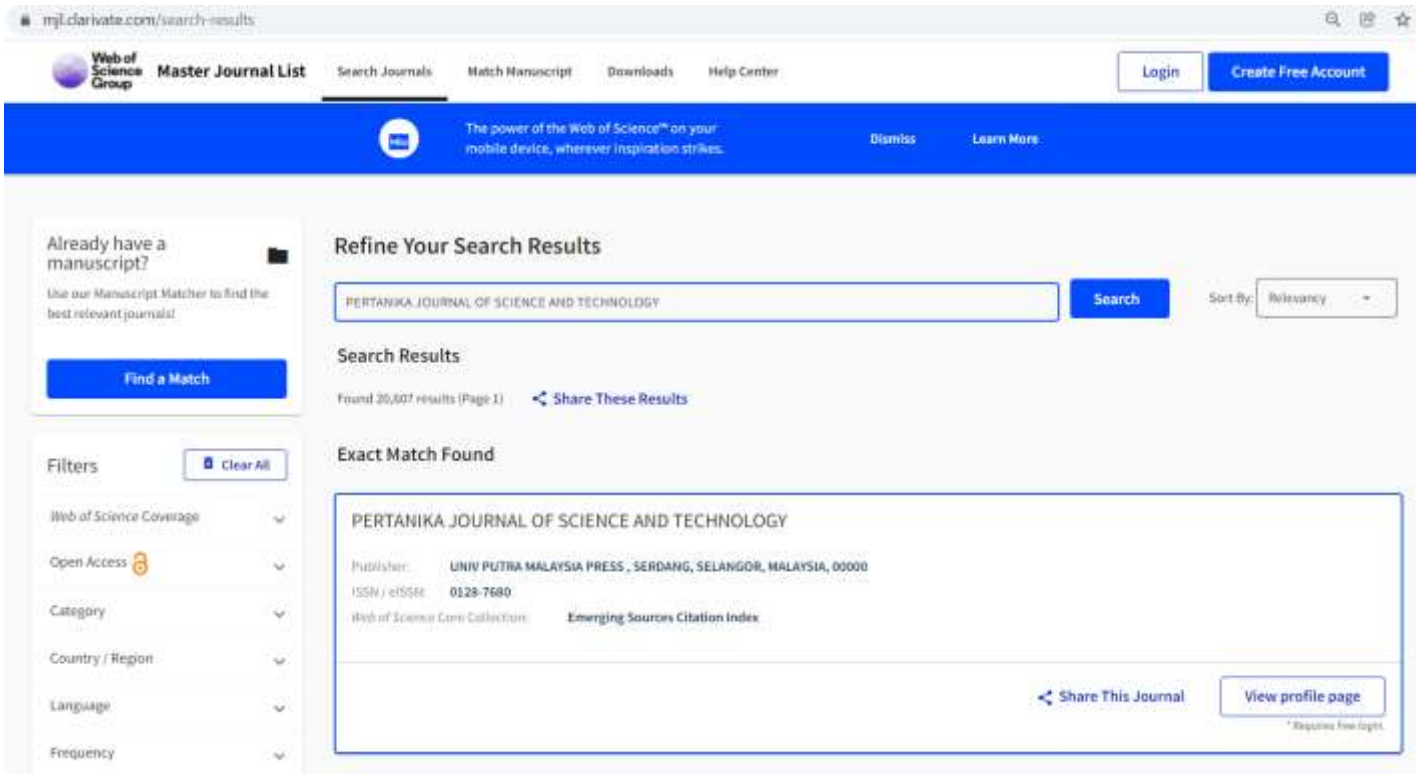

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Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis

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Keywords:	biodiesel, esterification, sulfuric acid, RSM, FFA
Abstract:	Non edible oil is among the favorable feedstock for biodiesel synthesis since it is economical and its utilization for energy resource doesn't cause competition with the food need. Among the prospective local non-edible vegetable oil in Indonesia is nyamplung seed oil (Calophyllum inophyllum). However, this oil cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (19.17%). The high free fatty acid (FFA) in oil will react with the base catalyst, resulting in soap as by product. To avoid this problem, FFA removal prior to nyamplung seed oil transesterification is necessary. There are some methods for FFA removal. In this work, FFA removal was performed using sulfuric acid catalyzed esterification. Experimental work and analysis using response surface methodology were conducted in this work. Esterification reaction was conducted using the fixed molar ratio of methanol and nyamplung seed oil of 30:1 and the reaction times of 120 minutes. The catalyst concentration was varied at 1%, 3%, 5%, and 7%, and the temperature variation was 40℃, 50℃, and 60℃. The reaction conversion was 78.18% and the FFA concentration was decreased to 4.01%, obtained at the reaction temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on the response surface methodology (RSM) was demonstrated that the quadratic model is the most suitable model in RSM for optimization of the FFA conversion in the future work. The RSM analysis resulted in the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g NSO, 119.95 minutes, respectively. The desirability ramp¬ was 1, which was in a good agreement with the experimental data. Extrapolation using RSM predict that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30. The predictive FFA conversion was 89.3%.

Running Title:

Free Fatty Acid Removal in Nyamplung Seed Oil

Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) by Esterification Reaction: Experimental and Response Surface Methodology Analysis

Abstract

Non edible oil is among the favorable feedstock for biodiesel synthesis since it is economical and its utilization for energy resource doesn't cause competition with the food need. Among the prospective local non-edible vegetable oil in Indonesia is nyamplung seed oil (*Calophyllum inophyllum*). However, this oil cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (19.17%). The high free fatty acid (FFA) in oil will react with the base catalyst, resulting in soap as by product. To avoid this problem, FFA removal prior to nyamplung seed oil transesterification is necessary. There are some methods for FFA removal. In this work, FFA removal was performed using sulfuric acid catalyzed esterification. Experimental work and analysis using response surface methodology were conducted in this work. Esterification reaction was conducted using the fixed molar ratio of methanol and nyamplung seed oil of 30:1 and the reaction times of 120 minutes. The catalyst concentration was varied at 1%, 3%, 5%, and 7%, and the temperature variation was 40°C, 50°C, and 60°C. The reaction conversion was 78.18% and the FFA concentration was decreased to 4.01%, obtained at the reaction temperature of 60°C and reaction time of 120 minutes. The polynomial model analysis on the response surface methodology (RSM) was demonstrated that the quadratic model is the most suitable model in RSM for optimization of the FFA conversion in the future work. The RSM analysis resulted in the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09°C, 1.98% g/g NSO, 119.95 minutes, respectively. The desirability ramp was 1, which was in a good agreement with the experimental data. Extrapolation using RSM predict that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30. The predictive FFA conversion was 89.3%.

Keywords: biodiesel; esterification; sulfuric acid; FFA; RSM

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. Thus far, fossil energy still dominates the energy supply all over the world (Ghasemian et al., 2020). However, the crude oil production in some countries shows a decline trend, which is not in balance with the energy need. Besides, utilization of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, which contribute to the global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilization have led to the increasing interest on the renewable energy research. In the recent days, many countries in the world implement the policy to use fossil fuel and biofuel blending to ensure the energy sustainability and security. Biodiesel is a viable biofuel which can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is nontoxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristic, high flash point which ensure its safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Mubarak Application of biodiesel/diesel fuel blends in diesel engine show a acceptable combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, to achieve complete conversion of one mol of triglycerides to alkyl esters; at least three moles of alcohol are required (Islam, 2014). The most common catalyst for biodiesel production is alkaline catalyst such as KOH, NaOH, or solid base catalyst. Transesterification process using alkaline catalyst is cheap and easy.

There are some potential biodiesel feedstocks in Indonesia, such as crude palm oil, jatropha oil, coconut oil, etc. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among the prospective local non edible oil in Indonesia for biodiesel production is nyamplung (*Calophyllum inophyllum*) seed oil (Musta et al., 2017; Silitonga et al., 2014). *Calophyllum inophyllum* is extensively planted in Indonesia and the nyamplung seed oil can be purchased from

the local farmers (Ong et al., 2019). Atabani & César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed satisfactory properties and good engine performance and emission in diesel machine.

However, crude nyamplung seed oil usually contains gum and high free fatty acid (FFA). The existence of high amount of FFA in feedstock is not desirable in alkaline catalyzed transesterification since it can react with the base catalyst, yielding the soap and diminish the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Thus, removal FFA as pre-treatment in high FFA nyamplung seed oil prior to the transesterification reaction to produce biodiesel is necessary. FFA removal in nyamplung seed oil can be conducted through esterification reaction using methanol using acid catalyst. Thus far, the study on the nyamplung seed oil esterification to reduce the FFA content has not been comprehensively carried out. Hence, in this work, removal of FFA in nyamplung seed oil through esterification of FFA with methanol in the presence of sulfuric acid catalyst was studied. The analysis using response surface methodology was also conducted to determine the optimal operation condition which resulted in the targeted value of FFA (2%).

MATERIALS AND METHOD

Materials

Material used in this work were: nyamplung seed oil (NSO), phosphoric acid (p.a., Merck), methanol (industrial grade, form local supplier), ethanol (p.a., Merck), KOH (p.a., Merck), oxalic acid (p.a., Merck), sulfuric acid (p.a., Merck), distilled water, and phenolphthalein indicator.

Method

Crude nyamplung seed oil (CNSO) contains high gum. Hence, prior to the esterification reaction, the crude NSO was first degummed using phosphoric acid to remove its gum content and resulted in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were characterized to reveal their properties, i.e: the fatty acid composition determination using Gas Chromatography-Mass Spectroscopy, density, viscosity, and acid value tests.

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using hot plate at 70°C. Sulfuric acid with the concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm aquadest (40-50°C in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated entirely. The two layers were formed. The top and bottom layers were refined NSO (RNSO) and gum, respectively. To remove the water content, the RNSO were then heated using oven at 105°C until it reached the constant weight.

FFA Removal

The FFA removal was conducted via esterification reaction with methanol in the presence of sulfuric acid. Refined NSO (RNSO) and methanol were weighed to obtain the molar ratio of NSO and methanol of 1:3. RNSO was introduced into the three neck flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at the identical temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into the reactor. The reaction temperatures were varied at 40°C, 50°C, and 60°C. Sulfuric acid catalyst was afterward added at a certain concentration (1%, 3%, 5%, 7% w/w NSO). Reaction was carried out at 120 minutes. A constant mixing using magnetic stirrer with the speed of 1000 rpm was performed to certify the homogeneous reaction. Sample was taken periodically every 10 minutes. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples were calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

Response Surface Methodology

Response Surface Methodology using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the box-behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic were evaluated to determine the most appropriate model for optimization. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of crude nyamplung seed oil (CNSO) and refined nyamplung seed oil (RNSO) which has undergone degumming process were demonstrated in Table 1:

Table 1

Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

Composition of fatty acid determination using GC-MS was exhibited in Table 2. Based on this composition, the molecular weight of nyamplung seed oil can be calculated. It was found that NSO molecular weight was 869.74 g/mol. It was found that the most dominant fatty acid in NSO were oleic acid and linoleic acids. It is in a good agreement with the fatty acid composition of NSO found by Aparamarta et al. (2020).

Table 2

Nyamplung Seed Oil (NSO) Fatty Acid Composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55
Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

FFA (free fatty acid) removal was conducted via esterification reaction of RNSO and methanol in the presence of sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied at 1%, 3%, 5%, dan 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40°C, 50°C, and 60°C. The reaction was run for 120 minutes. The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

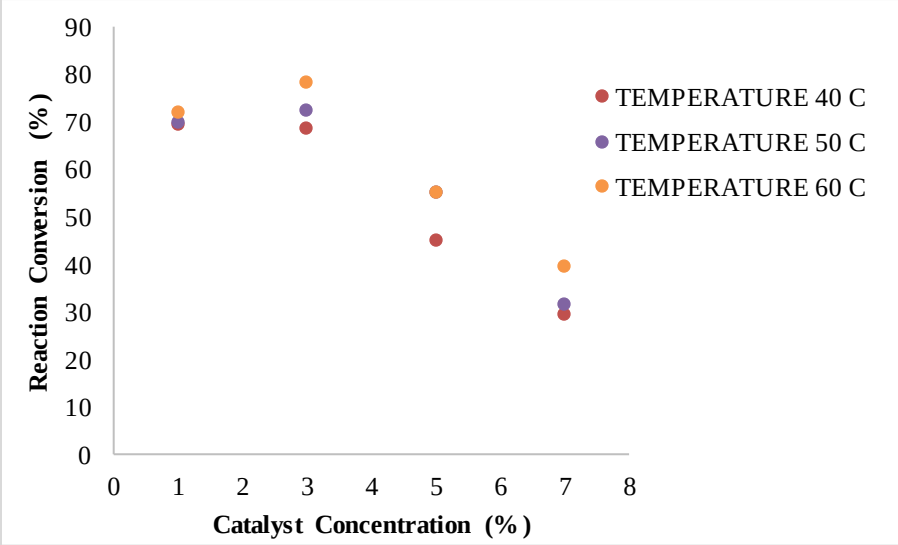

Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of Oil to Methanol of 1:30

It can be observed in Figure 1, reaction conversion increased at the catalyst concentration 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in the higher possibility of the reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the higher reaction concentration (5% to 7%), the apparent reaction conversion declined since the excessive amount of catalyst could provoke the side reaction and reduced the FFA conversion (Widiarti et al., 2017). The excessive employment of catalyst will correspondingly bring about the difficulty and higher cost in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the

temperature of 60°C with the reaction time of 120 minutes. The FFA content of such the operation condition was 4.01%.

3. 2. Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that, the higher reaction temperature, the higher removal of FFA occurred. This phenomenon was due to the fact that the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increasing of the reaction temperature raised the FFA conversion. This fact was also in agreement with the Arrhenius Law which states that the reaction rate is equivalent with the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. In accordance with the Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature risen.

It was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 – 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. The best conversion was achieved at the catalyst concentration of 3%, molar ratio oil to methanol oif 1:30, reaction temperature of 60°C, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal of FFA in kapok randu seed oil using methanol reactant and sulfuric acid catalyst was 60°C and reaction time of 120 minutes (Kusumaningtyas et al., 2019).

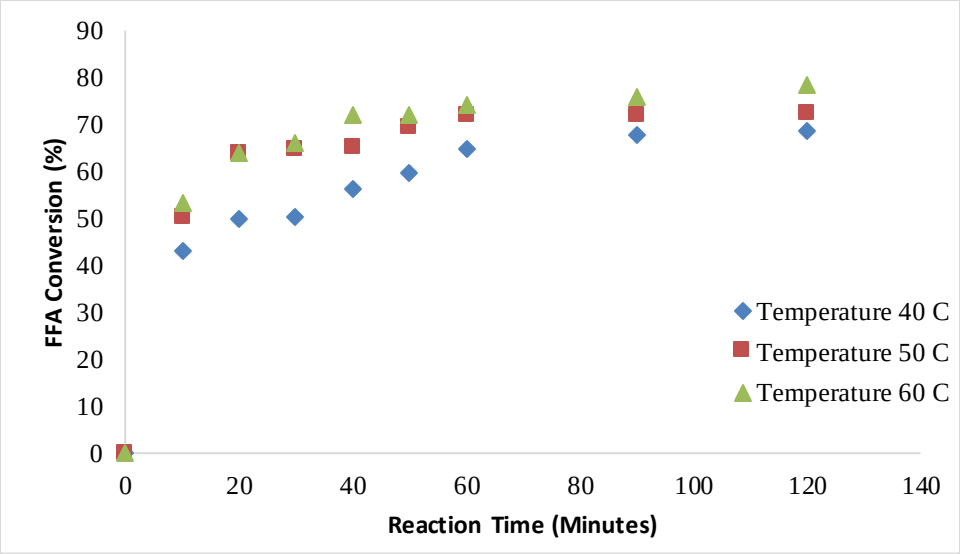

Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of Oil and Methanol of 1:30

Response Surface Methodology (RSM) Analysis

The result of the FFA removal was still under the targeted value of FFA content (below 2%). Thus, it was important to enhance the reaction conversion in the future work. The optimization using response surface methodology (RSM) will be beneficial for designing the reaction condition to achieve the targeted reaction conversion. Response surface methodology (RSM) a set of mathematical and statistical tools which can used for developing empirical model which correlate the reaction conversion or the yield of product with the significant process parameters (Veljković et al., 2019). Application of this tool has been found to be beneficial to reduce the experimental cost (J. Liu et al., 2018). However, there are several models provided for the optimization using RSM. Hence, the suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. The similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this work, the best polynomial model will be useful to be applied in the future work for designing the experiment condition and improving the conversion of the reaction. To select the model, combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification using sulfuric acid catalyst were investigated. Experiments with the different combination of the three variables were conducted

and calculated statistically using experimental design which was based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial. This full factorial design (Rodríguez-Ramírez et al., 2020). This full factorial design is the most commonly applied in RSM optimization (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Tabel 3
Experimental Design Using Box-Behnken Methodology (BBD) which Equipped with the Experimental Data and Predictive Result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25
2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The compatibility of the model with the experimental data was examined to determine the most appropriate model for conducting the response result prediction. The four polynomials models, namely linear, interactive (2FI), quadratic, and cubic were used to predict the response variable to the experimental data. Two types of tests, i.e., sequential model sum of squares and

model summary were used as the basic for the polynomial model determination which is suitable for optimizing the FFA conversion, as shown in Table 4 and 5, respectively.

Table 4

Sequential Model Sum of Squares Test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Qubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						
Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Qubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Tabel 5

Model Summary Test

Component	Std. Dev	R^2	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content						
Linear	**0.0250**	-	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	-	0.2604	-0.8490	-	0.9989
Quadratik	**0.0221**	-	**0.9172**	-	**Suggested**	**0.0221**
Qubic	-	-	-	-	Aliased	-
Model summary of FFA Conversion						
Linear	**0.0249**	-	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	-	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	-	**0.9171**	-	**Suggested**	**0.0222**
Qubic	-	-	-	-	Aliased	-

Based on the result shown in Table 4 and 5, it was attained that the quadratic model was justified as the most suitable model for optimizing the FFA content and FFA conversion in the esterification using sulfuric acid catalyst. The basis of the selection of the quadratic model was the maximum value of R^2, adjusted R^2, predicted R^2, and the lowest p-value. Thus, the quadratic model was further analyzed using ANOVA. This finding is in line the result analysis of Maran & Priya (2015), which suggested that quadratic model was the most appropriate model.

The empirical model which was expressed using quadratic model with the interaction obtained from the experimental data based on the RSM was modified into polynomial equation. The final equation for FFA content and FFA conversion optimization are presented in the Eq. 1 dan Eq. 2, respectively.

$$\text{FFA Content (\%)} = 16.5 - 0.306\,A - 2.2\,B + 0.014\,C - 0.0059\,AB - 0.000042\,AC + 0.0005\,BC + 0.0026\,A^2 + 0.54\,B^2 - 0.00014\,C^2 \quad (1)$$

$$\text{FFA Conversion (\%)} = 10.63 + 1.66\,A + 11.91B - 0.081\,C + 0.032\,AB + 0.00026\,AC + 0.0026\,BC - 0.014\,A^2 - 2.94\,B^2 + 0.00075\,C^2 \quad (2)$$

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6

ANOVA Regression Model to Predict the FFA Conversion Using Sulfuric Acid Catalyst

Source	*Sum of square*	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	
X_{23}	0.0992	1	0.0992	0.0120	0.9197	
X_1^2	4.37	1	4.37	0.5278	0.5201	
X_2^2	315.17	1	315.17	38.08	0.0086	
X_3^2	1.04	1	1.04	0.1258	0.7463	
Residual	24.83	3	8.28			
Cor Total	1197.58	12				
Adeq prec	12.46					

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential which could cause the model unsuccessful to predict the value of response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision is the measure of the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. Ratio of 12.46 resulted in this work denoted that the inputted signal was appropriate.

Validation of the model capability in predicting is necessary to ensure the accuracy of model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the calculation using the model was close to the experimental data. It was indicated by the point of the response values of prediction and experimental just about the 45^o line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

The model suitability was further diagnosed by constructing a plot between the externally studied residuals with the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error which could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the result of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimization in the FFA esterification using sulfuric acid catalyst. The graphical illustration, termed response surface, is frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).

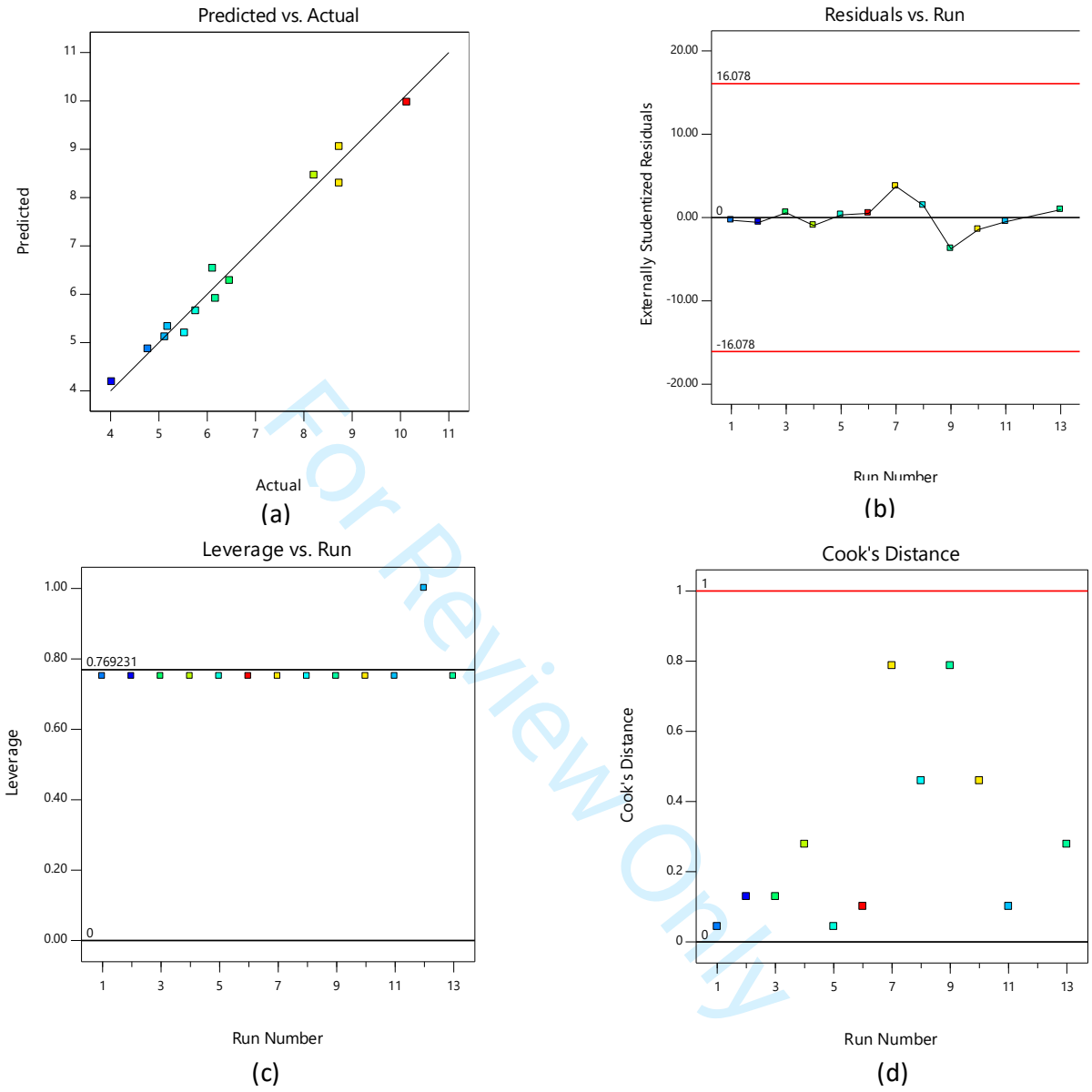

Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

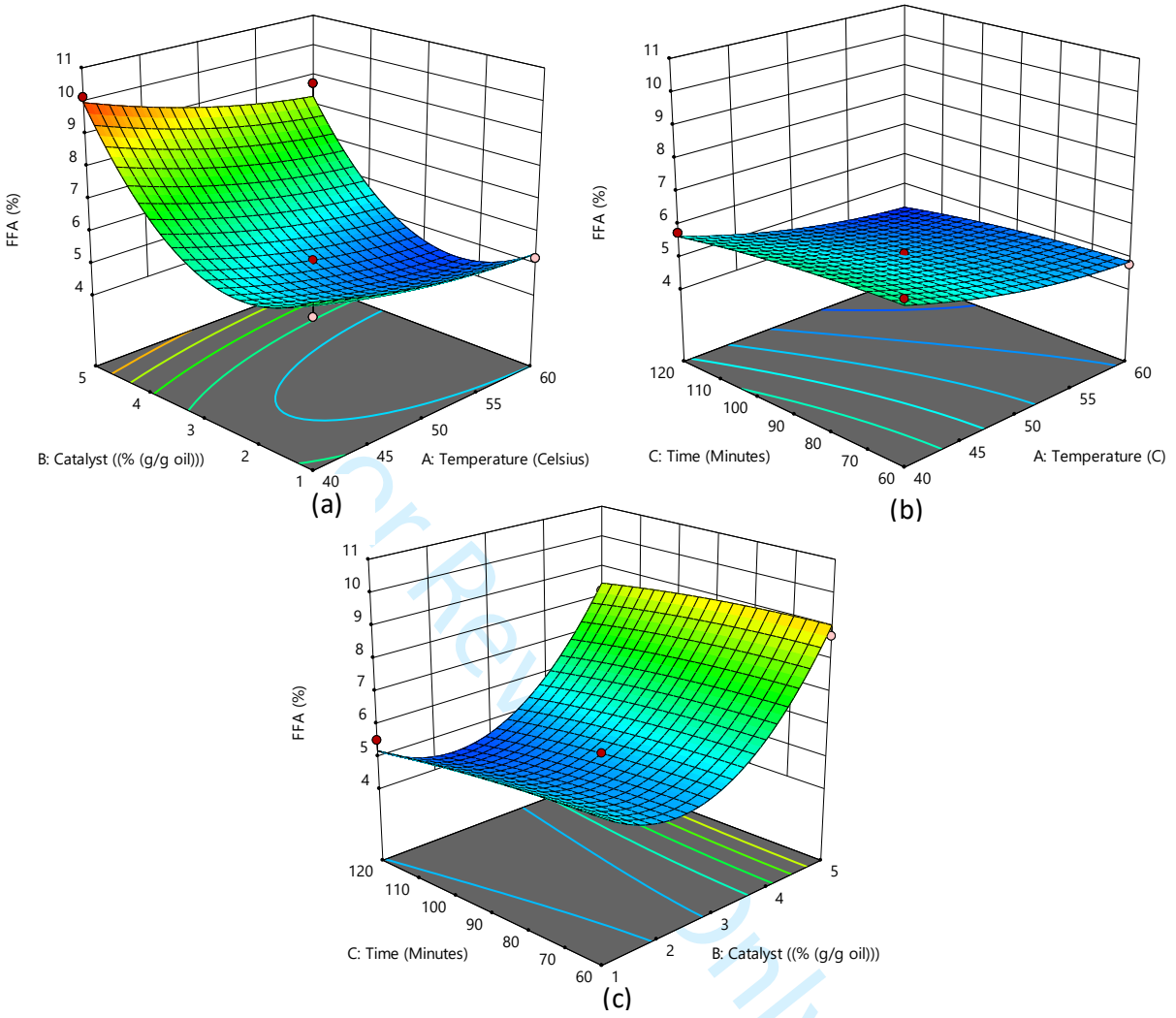

Figure 4. Three Dimensionals (3D) Response Surface of the Effect of the Process Condition to the FFA Content. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g NSO); and (c) Reaction Temperature = 50°C.

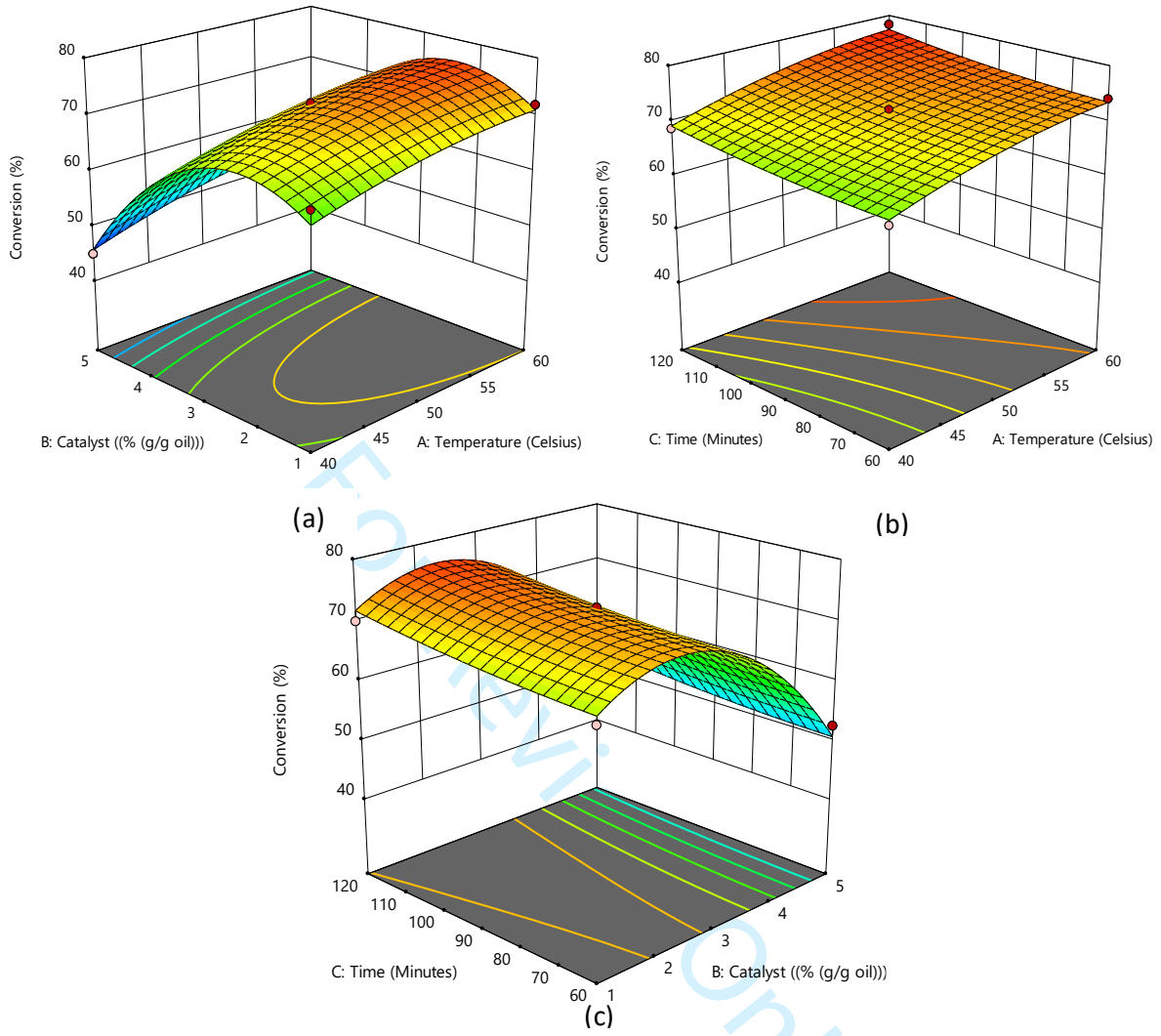

Figure 5. Three Dimensionals (3D) Response Surface of the Effect of the Process Condition to the FFA Conversion. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g NSO); and (c) Reaction Temperature = 50°C.

The significant variables affecting the FFA content and the FFA conversion were temperature and catalyst concentration as demonstrated in Figure 4 and 5, respectively. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to 60°C. Additionally, the increasing of catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, additional amount of catalyst employment did not resulted in the higher reaction conversion as well as the

FFA removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

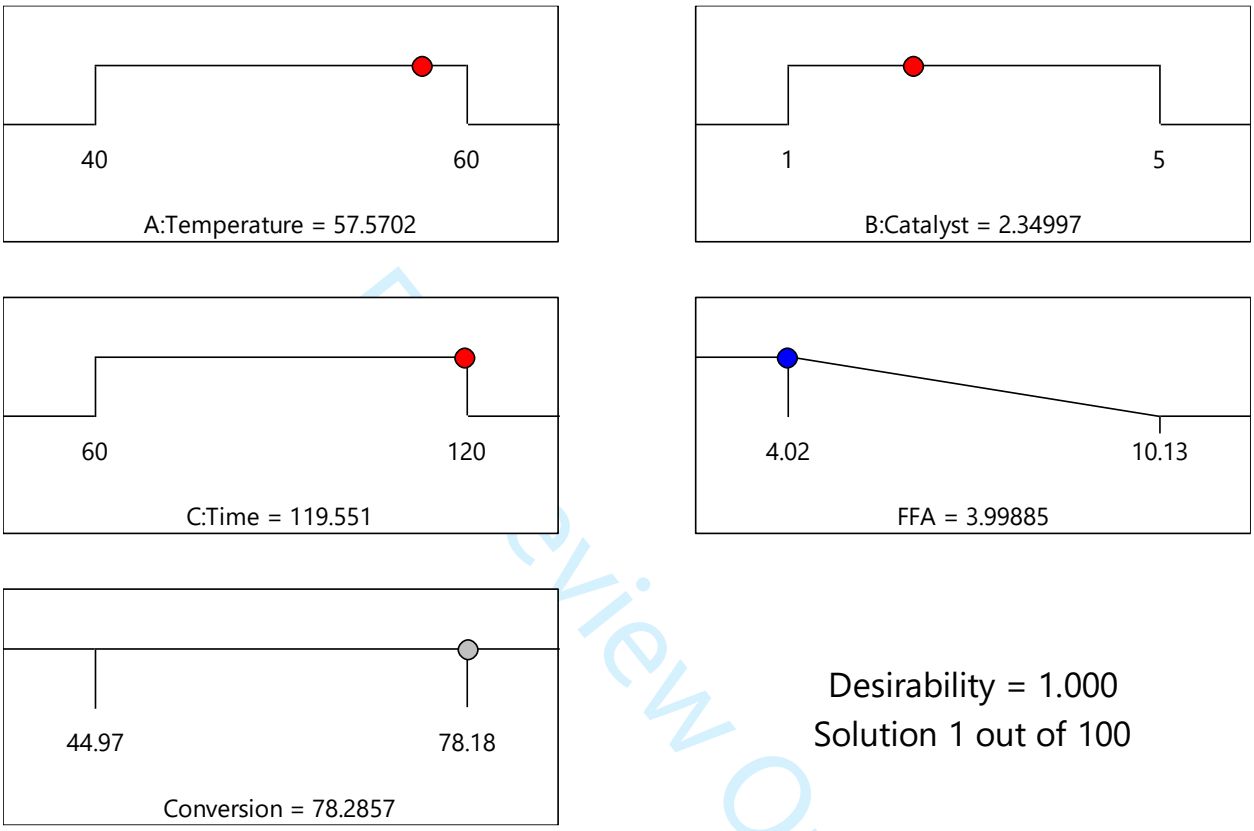

Figure 6. Optimization of FFA Conversion Using RSM (Quadratic Model)

In this work, Derringer Method was employed for the FFA conversion and FFA removal optimization in the esterification using sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as multi response problem based on Multicriteria Decision Making. In this case, desirability approach is often employed as a vigorous instrument for optimization in multi response system. Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided undesired response. On the other hand, the value 1 indicates to the optimal condition of the parameter evaluated (Amdoun et al., 2018).

Based on the RSM simulation, it was revealed that the optimum FFA conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 °C, catalyst concentration 1.98% g/g NSO, and reaction time of 119.95 minutes. At this operation condition, the value of the desirability ramp was 1 (Figure 6). The result fitted the experimental data.

To predict the operation condition to achieve the FFA content of maximum 2%, extrapolation using RSM was carried out. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration, and reaction time were 58.97°C, 3%, and 194.9 minutes, respectively, whereas, molar ratio of oil to methanol was fixed at 1:30. The FFA conversion achieved was estimated 89.3%.

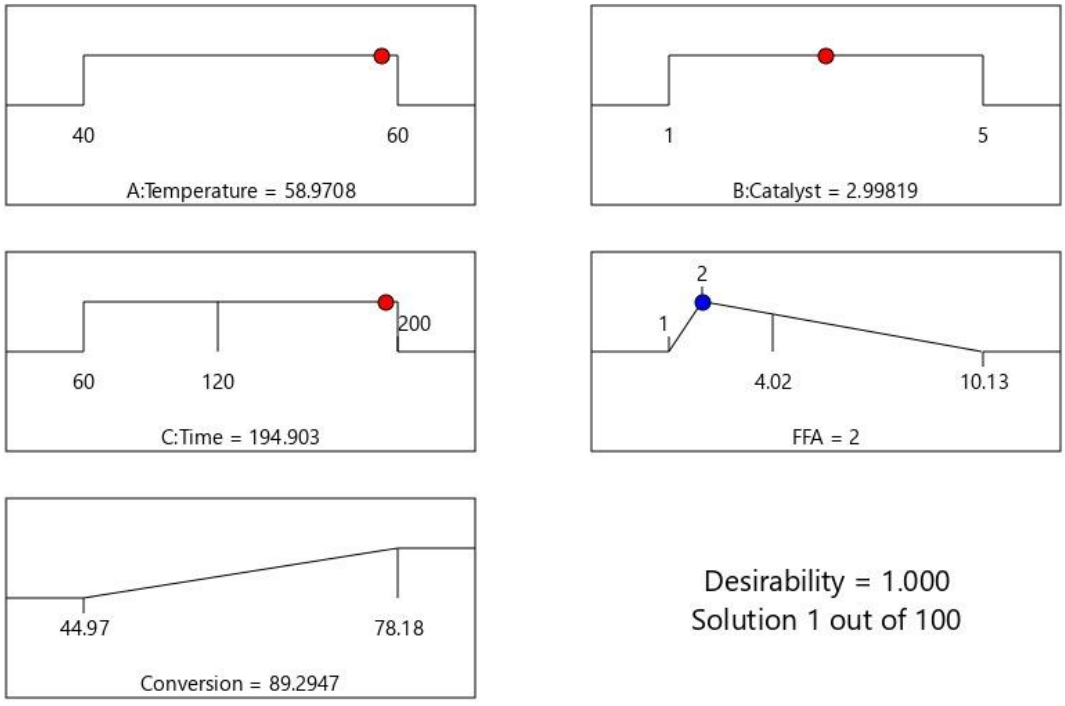

Figure 7. RSM Prediction of Operation Condition on the FFA Esterification Using Sulfuric Acid Catalyst to Decrease the FFA Content to 2%

The result has shown that RSM is simple and effective for process optimization. Furthermore, the combination of RSM and desirability function leads to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al., (2018).

CONCLUSION

The experimental work of FFA esterification in nyamplung seed oil with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition was the reaction temperature of 60℃, reaction time of 120 minutes, molar ratio of nyamplung seed oil (NSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. The RSM model analysis demonstrated that the quadratic model was the most suitable model for optimization of this process in the future work. The RSM optimization resulted in the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g NSO, 119.95 minutes, respectively. The desirability ramp was 1, which was in a good agreement with the experimental data. Extrapolation using RSM predict that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30. The predictive FFA conversion was 89.3%.

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24-May-2021

Dear Dr. Kusumaningtyas,

Manuscript ID JST-2591-2021 entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis" which you submitted to the Journal of Science and Technology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter. I invite you to respond to the reviewer(s)' comments and revise your manuscript.

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Comments to the Corresponding Author
Regarding the model what you choose RSM.
what for you fixed the goal of 2 % FFM Reduction.
What way you work differ from other published article in the same topic. I have seen more than enough. What is the experimental setup whether you check the values using experimental setup and validated with references. The Results should be discussed deeply to validate the data, but hardly not discussion.

Reviewer: 2 (with attachment)

Comments to the Corresponding Author
Overall the work is an interesting area for the vegetable oil research.

Reviewer: 3

Comments to the Corresponding Author
Table Of Comments
General
The present paper reviews the optimization of free fatty acid removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction.

-Suggestion to rewrite the title

Abstract
Conclusion- its missing.

Introduction
Include study of other acid catalyst.

Methodology
Line 34 page 4…what grade? Analytical?
Line 47-50 page 4…rewrite
Line 40 page 4 Method for characterization is missing.
Line 45 page 5 how many runs?

Discussion

Table 1&2-discuss
Table4 -Line Centre point? lack of fit? predicted r2?
Figure 4&5 …no discussion ..only results reported.
What is the novelty of this study? What is the significance of this study?

Conclusion

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Subject: Journal of Science and Technology - Decision on Manuscript ID JST-2591-2021 (AA)

Body: 24-May-2021

Dear Dr. Kusumaningtyas,

Manuscript ID JST-2591-2021 entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis" which you submitted to the Journal of Science and Technology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter. I invite you to respond to the reviewer(s)' comments and revise your manuscript.

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Once again, thank you for submitting your manuscript to the Journal of Science and Technology and I look forward to receiving your revision.

Sincerely,
Chief Executive Editor, Journal of Science and Technology

Reviewer(s)' Comments to Author:

Reviewer: 1

Comments to the Corresponding Author
Regarding the model what you choose RSM.
what for you fixed the goal of 2 % FFM Reduction.
What way you work differ from other published article in the same topic. I have seen more than enough. What is the experimental setup whether you check the values using experimental setup and validated with references. The Results should be discussed deeply to validate the data, but hardly not discussion.

Reviewer: 2 (with attachment)

Comments to the Corresponding Author
Overall the work is an interesting area for the vegetable oil research.

Reviewer: 3

Comments to the Corresponding Author
Table Of Comments
General
The present paper reviews the optimization of free fatty acid removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction.

-Suggestion to rewrite the title

Abstract
Conclusion- its missing.

Introduction
Include study of other acid catalyst.

Methodology
Line 34 page 4…what grade? Analytical?
Line 47-50 page 4…rewrite
Line 40 page 4 Method for characterization is missing.
Line 45 page 5 how many runs?

Discussion

Table 1&2-discuss
Table4 -Line Centre point? lack of fit? predicted r2?
Figure 4&5 …no discussion ..only results reported.
What is the novelty of this study? What is the significance of this study?

Conclusion

Rewrite

Date Sent: 24-May-2021

File 1: JST-2591-2021-MS-Rev-Kit---Comments-on-PDF--RW02-.pdf

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Comments on the manuscript JST-2591-2021 entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis"

The manuscript is in accordance to the journal scope, so it could be eligible in the future after the proposed revisions.

General
The present manuscript has deficiencies, which have to be improved before the manuscript acceptance.

In general, the similarity checking done via Turnitin software indicates 14% of similarity.

The main problems, not in order of significance, are summarized as follows.

Title

Suggest to revise the title, the study only focus on paddy straw instead of lignocellulosic biomass; which should shows data from various type of raw materials.

Abstract
The abstract contains all important information, however, it is too long for a journal paper, suggest to reduce according to the publisher guideline.

Introduction

2nd sentence; term Thus far is not suitable, suggest to revise.

Pg 3 Line 29/30; Double check the sentence; Mubarak Application of biodiesel/diesel fuel…

Materials and method

Method

The intro paragraph seems not relevant as it is a repetition information, suggest to remove.

Result and Discussion

CNSO and RNSO Characterization
Table 1: No explanation or discussion. The paragraph written is not complete.

Table 2: Define the NSO sample use for this analysis. Why no comparison done between RNSO & CNSO?

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

1st paragraph; double check the molar ratio of RNSO: methanol written in this paragraph. Different from the methods.

Figure 1; Missing data for 5% at 50degC or is it overlapped?

Pg 8 Line 4/5: "The FFA content of such the operation condition was 4.01%." Suggest to further explain the sentence.

Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

Paragraph 2 should mention which figure the explanation is about, double check the type error in this paragraph.

Response Surface Methodology (RSM) Analysis

In the RSM, should justify why catalyst concentration, temperature, and reaction time are significant variable for the optimization.

Pg 10; Line 7; "This full factorial design (Rodríguez-Ramírez et al., 2020)." Further clarify the sentence.

Pg 10; Line 50; The content of this paragraph is a repetition information in the earlier paragraph.

Table 5; no data for R2, Why? What is the normal R2 value for the esterification process?

Figure 6 and 7 should further explain and discussed.

Suggest to resize all the figures, using lots of spaces.

Conclusion
Conclusion is reflecting with the manuscript content.

In summary, this manuscript presents interesting data; thus, this manuscript could be possible recommended in future for publication after the proposed revision.

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Journal of Science and Technology - Manuscript ID JST-2591-2021.R1

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08-Jun-2021

Dear Dr. Kusumaningtyas,

Your manuscript entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis" has been successfully submitted online and is presently being given full consideration for publication in the Journal of Science and Technology.

Your manuscript ID is JST-2591-2021.R1.

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Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis

Journal:	*Journal of Science and Technology*
Manuscript ID	JST-2591-2021.R1
Manuscript Type:	Regular Article
Scope of the Journal:	Biomass energy technology < Energy industry < APPLIED SCIENCES AND TECHNOLOGIES, Wood & non wood-based forest products < Resource-based industry < APPLIED SCIENCES AND TECHNOLOGIES, Oil < Resource-based industry < APPLIED SCIENCES AND TECHNOLOGIES, By-product utilisation < Agriculture engineering < ENGINEERING SCIENCES
Keywords:	biodiesel, esterification, sulfuric acid, RSM, FFA
Abstract:	Non edible oil is among the favorable feedstock for biodiesel synthesis since it is economical and its utilization for energy resource doesn't cause competition with the food need. Among the prospective local non-edible vegetable oil in Indonesia is nyamplung seed oil (Calophyllum inophyllum). However, this oil cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (19.17%). The high free fatty acid (FFA) in oil will react with the base catalyst, resulting in soap as by product. To avoid this problem, FFA removal prior to nyamplung seed oil transesterification is necessary. There are some methods for FFA removal. In this work, FFA removal was performed using sulfuric acid catalyzed esterification. Experimental work and analysis using response surface methodology were conducted in this work. Esterification reaction was conducted using the fixed molar ratio of methanol and nyamplung seed oil of 30:1 and the reaction times of 120 minutes. The catalyst concentration was varied at 1%, 3%, 5%, and 7%, and the temperature variation was 40℃, 50℃, and 60℃. The reaction conversion was 78.18% and the FFA concentration was decreased to 4.01%, obtained at the reaction temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on the response surface methodology (RSM) was demonstrated that the quadratic model is the most suitable model in RSM for optimization of the FFA conversion in the future work. The RSM analysis resulted in the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g NSO, 119.95 minutes, respectively. The desirability ramp¬ was 1, which was in a good agreement with the experimental data. Extrapolation using RSM predict that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30. The predictive FFA conversion was 89.3%.

Running Title:

Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil

Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

Abstract

Nyamplung seed (*Calophyllum inophyllum L.*) oil is a prospective non-edible vegetable oil as biodiesel feedstock, but it cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalyzed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18% and the FFA concentration was decreased to 4.01% at the temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable model for the FFA conversion optimization. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% can be obtained at the temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30.

Keywords: biodiesel; esterification; sulfuric acid; FFA; RSM; box-behnken; quadratic model

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. To date, fossil energy still dominates the energy supply all over the world (Ghasemian et al., 2020). However, the crude oil production in some countries shows a decline trend, which is not in balance with the energy need. Besides, utilization of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, which contribute to the global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilization have led to the increasing interest on the renewable energy research. In the recent days, many countries in the world implement the policy to use fossil fuel and biofuel blending to ensure the energy sustainability and security. Biodiesel is a viable biofuel which can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is nontoxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristic, high flash point which ensure its safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Application of biodiesel/diesel fuel blends in diesel engine show an acceptable combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, to achieve complete conversion of one mol of triglycerides to alkyl esters; at least three moles of alcohol are required (Islam, 2014). The most common catalyst for biodiesel production is alkaline catalyst such as KOH, NaOH, or solid base catalyst. Transesterification process using alkaline catalyst is cheap and easy.

There are some potential biodiesel feedstocks in Indonesia, such as crude palm oil, jatropha oil, coconut oil, etc. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among the prospective local non edible oil in Indonesia for biodiesel production is nyamplung (*Calophyllum inophyllum L.*) seed oil (Musta et al., 2017; Silitonga et al., 2014).

Calophyllum inophyllum L is extensively planted in Indonesia and the nyamplung seed oil can be purchased from the local farmers (Ong et al., 2019). Atabani & César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed satisfactory properties and good engine performance and emission in diesel machine.

However, crude nyamplung seed oil (CNSO) usually contains gum and high free fatty acid (FFA). The existence of high amount of FFA in feedstock is not desirable in alkaline catalyzed transesterification since it can react with the base catalyst, yielding the soap and diminish the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Generally, the maximum tolerable amount of FFA in base-catalyzed transesterification is 2%. Thus, a pre-treatment step to reduce the FFA content in nyamplung seed oil to maximum level of 2% prior to transesterification reaction is necessary. FFA removal in CNSO can be conducted through esterification reaction using methanol in the presence of acid catalyst. There are several types of acid catalyst for FFA esterification. They are categorized into the homogenous acid catalysts, for instance sulfuric acid, para-toluene sulfonic acid, phosphoric acid, and hydro, and HCl (Harun et al., 2018; Murad et al., 2018) and the heterogenous ones, such as Amberlyst 15, sulfated zirconia, niobic acid, zeolite, and tin (II) chloride (Banchero & Gozzelino, 2018; Dal Pozzo et al., 2019; Kusumaningtyas et al., 2014) Homogenous catalyst, particularly sulfuric acid, has been found as an efficient and economical catalyst for FFA esterification both at laboratory and industrial scales (Banani et al., 2015; Chai et al., 2014; Gebremariam & Marchetti, 2018). Therefore, sulfuric acid was selected as catalyst for the FFA removal via esterification reaction of CNSO oil in this work. The investigation included experimental work and the analysis using response surface methodology (RSM) to determine the optimal operation condition which yielded the targeted FFA final value of 2%. The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction. The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimization. The study on the FFA esterification in CNSO in the presence of sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimization has never been reported in the literature.

MATERIALS AND METHOD

Materials

Material used in this work were: crude nyamplung seed oil (CNSO), phosphoric acid (p.a., Merck), methanol (industrial grade, form local supplier), ethanol (analytical grade, from Merck), KOH (analytical grade, from Merck), oxalic acid (analytical grade, from Merck), sulfuric acid (analytical grade, from Merck), distilled water (analytical grade, from local supplier), and phenolphthalein indicator (analytical grade, from Merck).

Methods

Nyampung Seed Oil Characterization

Prior to the esterification reaction, the crude nyamplung seed oil (CNSO) was first degummed using phosphoric acid to remove its gum content and resulted in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were then characterized to reveal their properties. The fatty acid composition was determined using Gas Chromatography-Mass Spectroscopy (GC-MS Perkin Elmer, GC Clarus 680, MS Clarus SQ 8T) with the similar method to our previous work (Kusumaningtyas et al., 2016). Density measurement was conducted using pycnometer (Taghizade, 2016). Viscosity determination was carried out using viscometer bath Stanhope-Seta KV6 tube 350 CFO. Acid value tests was accomplished based on the AOCS acid-base titration method (Banchero & Gozzelino, 2018).

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using hot plate at 70℃. Sulfuric acid with the concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm distilled water (40-50℃ in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated entirely. The two layers were formed. The top and bottom layers were refined nyamplung seed oil (RNSO) and gum, respectively. To remove the water content, the RNSO were then heated using oven at 105℃ until it reached the constant weight.

FFA Removal

The FFA removal was conducted via esterification reaction with methanol employing sulfuric acid. RNSO and methanol were weighed to obtain the molar ratio of RNSO and methanol of 1:30. RNSO was introduced into the three necks flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at the identical temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into the reactor. The reaction temperatures were varied at 40℃, 50℃, and 60℃. Sulfuric acid catalyst was afterward added at a certain concentration (1%, 3%, 5%, 7% w/w RNSO). The reaction was carried out for 120 minutes. A constant mixing using magnetic stirrer with the speed of 1000 rpm was performed to certify the homogeneous reaction. The total experimental running was 7 experiments with different operation condition. Sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples were calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

Response Surface Methodology

Response Surface Methodology using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the box-behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic were evaluated to determine the most appropriate model for optimization. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of crude nyamplung seed oil (CNSO) and refined nyamplung seed oil (RNSO) which has undergone degumming process were demonstrated in Table 1. Degumming process aims for reducing the gum content. Besides, degumming has also brought about a better characteristic of the oil feedstock. It can be observed in Table 1, the density viscosity, acid number, and acidity of the RNSO were lower than CNSO. The decreasing value of density happened due to the losses of some heavy compound such as gum. The degumming process also caused a lighter color of the oil. It was due to the removal of the compounds which significantly

affected the oil color (Lamas et al., 2016). Degumming process has shown a better characteristic of the oil feedstock, leading to an effective transesterification reaction and a higher quality of biodiesel product.

Table 1

Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

Composition of fatty acid in CNSO was determined using GC-MS and the result was exhibited in Table 2. Based on this composition, the molecular weight of CNSO can be calculated. It was found that CNSO molecular weight was 869.74 g/mol and the most dominant fatty acid in CNSO were oleic acid and linoleic acids. It is in a good agreement with the fatty acid composition found by Aparamarta et al. (2020). Fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process didn't significantly change the fatty acid composition.

Table 2

Crude Nyamplung Seed Oil (CNSO) Fatty Acid Composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55

Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

FFA (free fatty acid) removal was conducted via esterification reaction of RNSO and methanol in the presence of sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied at 1%, 3%, 5%, dan 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40℃, 50℃, and 60℃. Encinar et al. (2021) suggested the sulfuric acid catalyst concentration of 0.5 – 2% for the feedstock with FFA content of 10.7%. The higher sulfuric catalyst concentration can be employed for the higher acidic vegetable oils. The molar ratio of oil to methanol referred to Chai et al. (2014) that recommended the molar ratio of oil to methanol in the range of 1:20 to 1:60. Specifically, Marchetti & Errazu (2008) proposed the molar ratio of 1:30 as the optimal condition. On the other hand, the reaction temperature ratio was adjusted to the boiling point of the methanol. The reaction was run for 120 minutes as suggested by Chai et al. (2014). The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

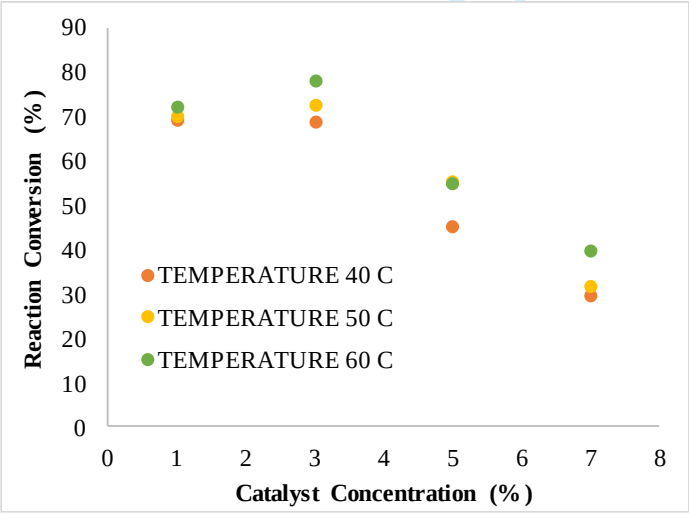


Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of RNSO to Methanol of 1:30

It can be observed in Figure 1, reaction conversion increased at the catalyst concentration 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in the higher possibility of the reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the higher reaction concentration (5% to 7%), the apparent reaction conversion declined since the excessive amount of catalyst could provoke the side reaction and reduced the FFA conversion (Widiarti et al., 2017). The excessive employment of catalyst will correspondingly bring about the difficulty and higher cost in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the temperature of 60°C with the reaction time of 120 minutes. The FFA content of such the operation condition was 4.01%. This value has not satisfied yet the maximum allowable FFA content of 2% for the transesterification reaction. Therefore, further observation was conducted at the different temperature and reaction time.

3. 2. Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that, the higher reaction temperature, the higher removal of FFA occurred. This phenomenon was due to the fact that the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increasing of the reaction temperature raised the FFA conversion. This fact was also in agreement with the Arrhenius Law which states that the reaction rate is equivalent with the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. In accordance with the Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature risen.

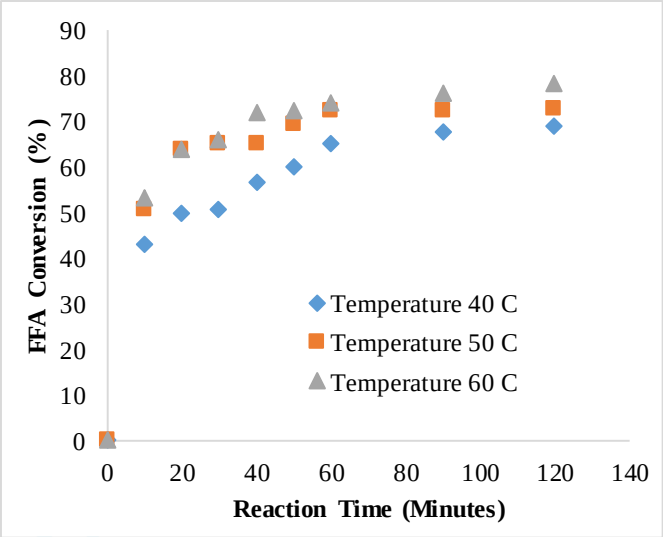


Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of RNSO and Methanol of 1:30

As shown in Figure 2, it was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 – 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. Based on catalyst concentration alteration (Figure 1) as well as the temperature and reaction time variation (Figure 2), it was revealed that the best conversion was achieved at the catalyst concentration of 3%, molar ratio of RNSO to methanol of 1:30, reaction temperature of 60℃, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal in kapok randu seed oil using methanol reactant and sulfuric acid catalyst was 60℃ and reaction time of 120 minutes (Kusumaningtyas et al., 2019). Among the promising way to enhance the reaction conversion is by increasing the reaction temperature to 65℃ and applying higher molar ratio of the reactants as accomplished by Chai et al. (2014). In this work, the lowest FFA content obtained among all the experiments conducted was 4.01%. It didn't match with the standard limitation of FFA content for base catalyzed transesterification (2%). Therefore, response surface methodology optimization was then carried out to predict the optimum operation condition of the esterification reaction which can yield the 2% FFA content of RNSO.

Response Surface Methodology (RSM) Analysis

The result of the FFA removal was under the targeted value of FFA content (maximum 2%). Thus, optimization using response surface methodology (RSM) will be beneficial for designing the operation condition to achieve the targeted conversion. RSM is a set of mathematical and statistical tools which can be used for developing empirical model which correlate the reaction conversion or the yield of product with the significant process parameters (Veljković et al., 2019). Application of this tool has been found to be valuable to reduce the experimental cost (J. Liu et al., 2018). However, there are several models provided for the optimization using RSM. Hence, the suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. The similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this study, the best polynomial model will be useful to be applied in the future work for designing the experiment condition and improving the conversion of the reaction. To select the model, combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification in RNSO using sulfuric acid catalyst were investigated. These variables were used for the optimization using RSM since they were the main parameters studied in experimental work. Experiments with the different combination of the three variables were conducted and calculated statistically using experimental design which was based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial (Rodríguez-Ramírez et al., 2020). This full factorial design is the most commonly applied in RSM optimization (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Tabel 3

Experimental Design Using Box-Behnken Methodology (BBD) which Equipped with the Experimental Data and Predictive Result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25

2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The four polynomial models, namely linear, interactive (2FI), quadratic, and cubic were used to predict the response variable to the experimental data. Two types of tests, i.e., sequential model sum of squares and model summary were used as the basic for the polynomial model determination which is suitable for optimizing the FFA conversion. The result is shown in Table 4 and 5, respectively.

Table 4

Sequential Model Sum of Squares Test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Qubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						

Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Qubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Tabel 5

Model Summary Test

Component	Std. Dev	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content					
Linear	**0.0250**	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	0.2604	-0.8490	-	0.9989
Quadratik	**0.0221**	**0.9172**	**-**	**Suggested**	**0.0221**
Qubic	-	-	-	Aliased	-
Model summary of FFA Conversion					
Linear	**0.0249**	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	**0.9171**	**-**	**Suggested**	**0.0222**
Qubic	-	-	-	Aliased	-

Based on the result shown in Table 4 and 5, it was acquired that the quadratic model was justified as the most suitable model for optimizing the FFA content and conversion in the esterification using sulfuric acid catalyst. The basis of the selection of the quadratic model was the lowest p-value, the highest value of adjusted R^2, and the highest value of predicted R^2.

Tabel 4 reveals that the quadratic model provided the lowest p-value. Table 5 shows that the highest value of adjusted R^2 was provided by the quadratic model. Meanwhile, the predicted R^2 for the quadratic model didn't appear in Table 5 since the value was precisely closed to 1. In contrast, the values of actual R^2 were not presented in Table 5 since this table depicted the summary of the model test. The actual R^2 values were advanced investigated based on the values of predicted R^2. Based on the values of the p-value, adjusted R^2, and predicted R^2 attained, the quadratic model was found as the most suitable model and further analyzed using ANOVA. This finding is in line the result analysis of Maran & Priya (2015), which suggested that quadratic model was the most appropriate model.

The empirical model which was expressed using quadratic model with the interaction obtained from the experimental data based on the RSM was modified into polynomial equation. The final equation for FFA content and FFA conversion optimization are presented in the Eq. 1 dan Eq. 2, respectively.

$$\text{FFA Content (\%)} = 16.5 - 0.306\,A - 2.2\,B + 0.014\,C - 0.0059\,AB - 0.000042\,AC + 0.0005\,BC + 0.0026\,A^2 + 0.54\,B^2 - 0.00014\,C^2 \quad (1)$$

$$\text{FFA Conversion (\%)} = 10.63 + 1.66\,A + 11.91B - 0.081\,C + 0.032\,AB + 0.00026\,AC + 0.0026\,BC - 0.014\,A^2 - 2.94\,B^2 + 0.00075\,C^2 \quad (2)$$

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6

ANOVA Regression Model to Predict the FFA Conversion Using Sulfuric Acid Catalyst

Source	*Sum of square*	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	

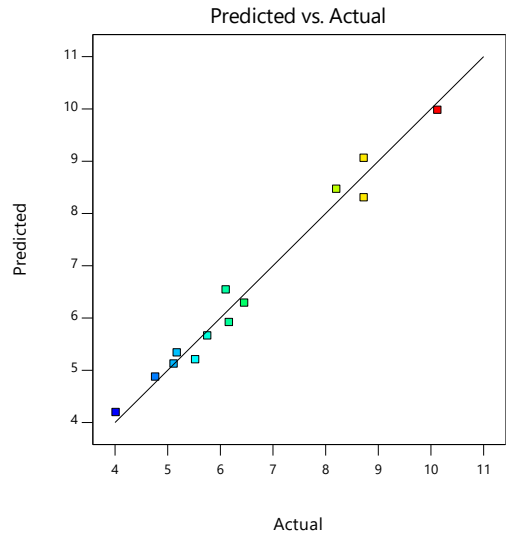
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	
X_{23}	0.0992	1	0.0992	0.0120	0.9197	
X_1^2	4.37	1	4.37	0.5278	0.5201	
X_2^2	315.17	1	315.17	38.08	0.0086	
X_3^2	1.04	1	1.04	0.1258	0.7463	
Residual	24.83	3	8.28			
Cor Total	1197.58	12				
Adeq prec	12.46					

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential which could cause the model unsuccessful to predict the value of response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision is the measure of the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. Ratio of 12.46 resulted in this work denoted that the inputted signal was appropriate.

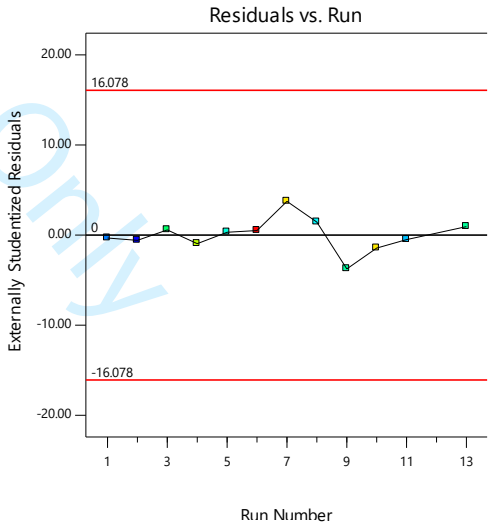
Validation of the model capability in predicting is necessary to ensure the accuracy of model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the calculation

using the model was close to the experimental data. It was indicated by the point of the response values of prediction and experimental just about the 45^{o} line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

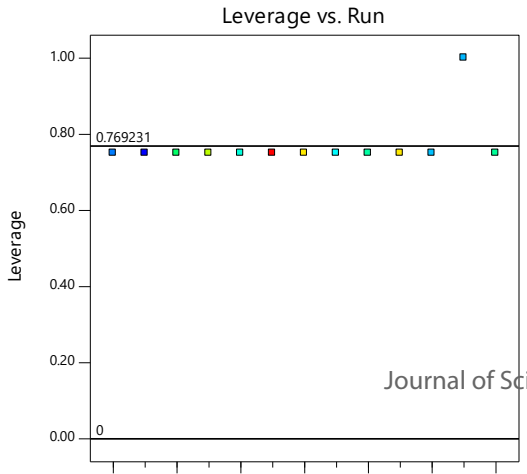
The model suitability was further diagnosed by constructing a plot between the externally studied residuals with the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error which could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the result of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimization in the FFA esterification using sulfuric acid catalyst. The graphical illustration, termed response surface, is frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).



(a)



(b)



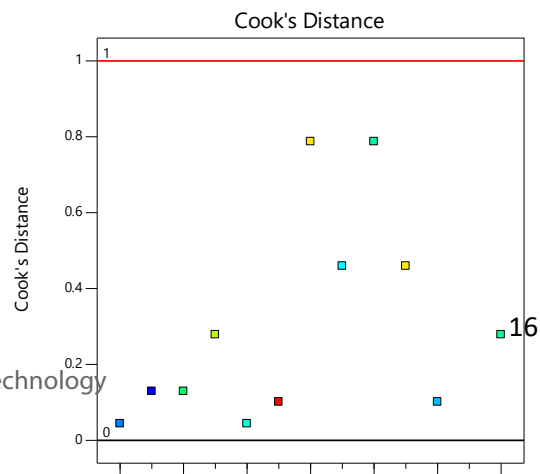


Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

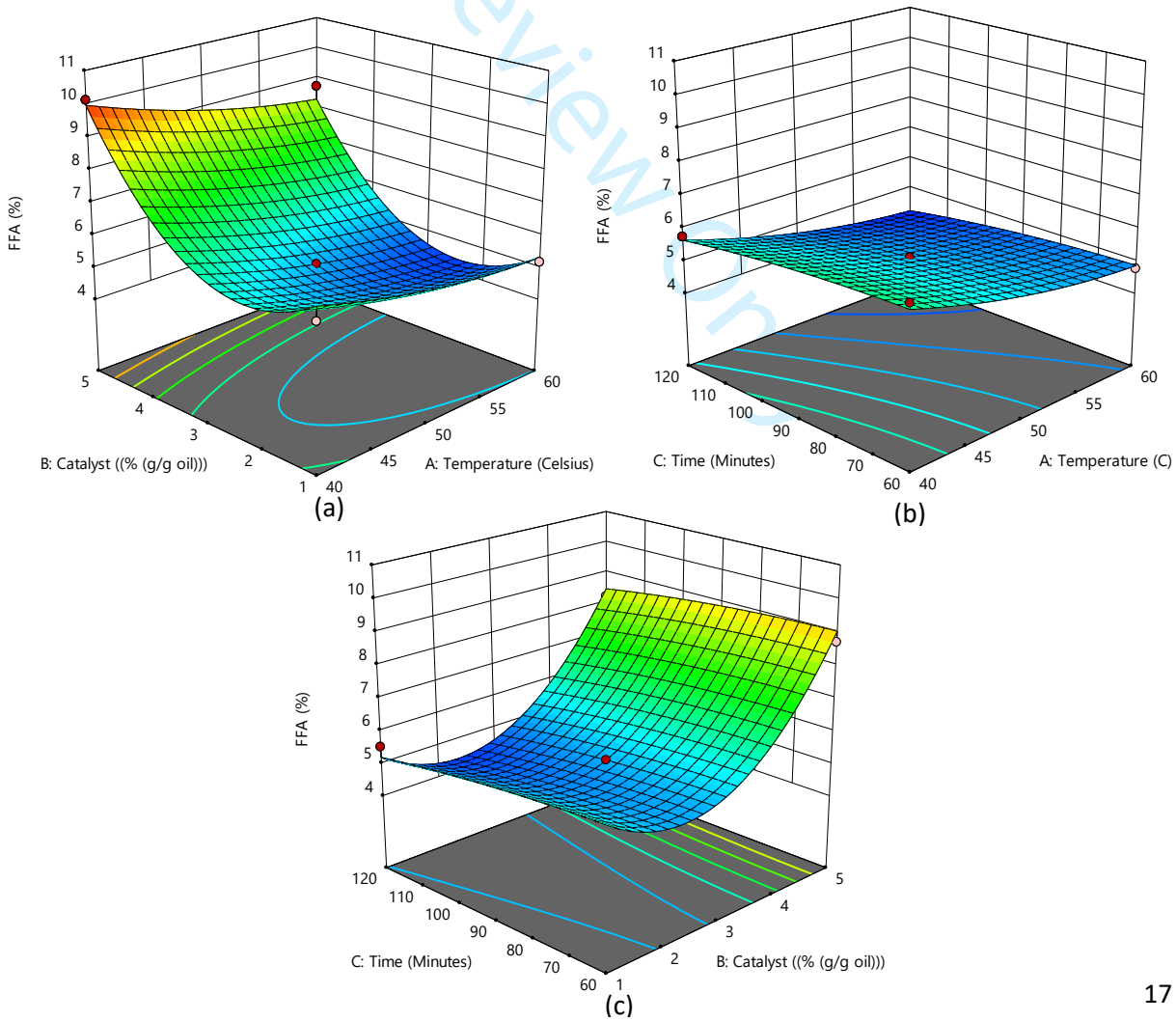


Figure 4. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Content. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50℃.

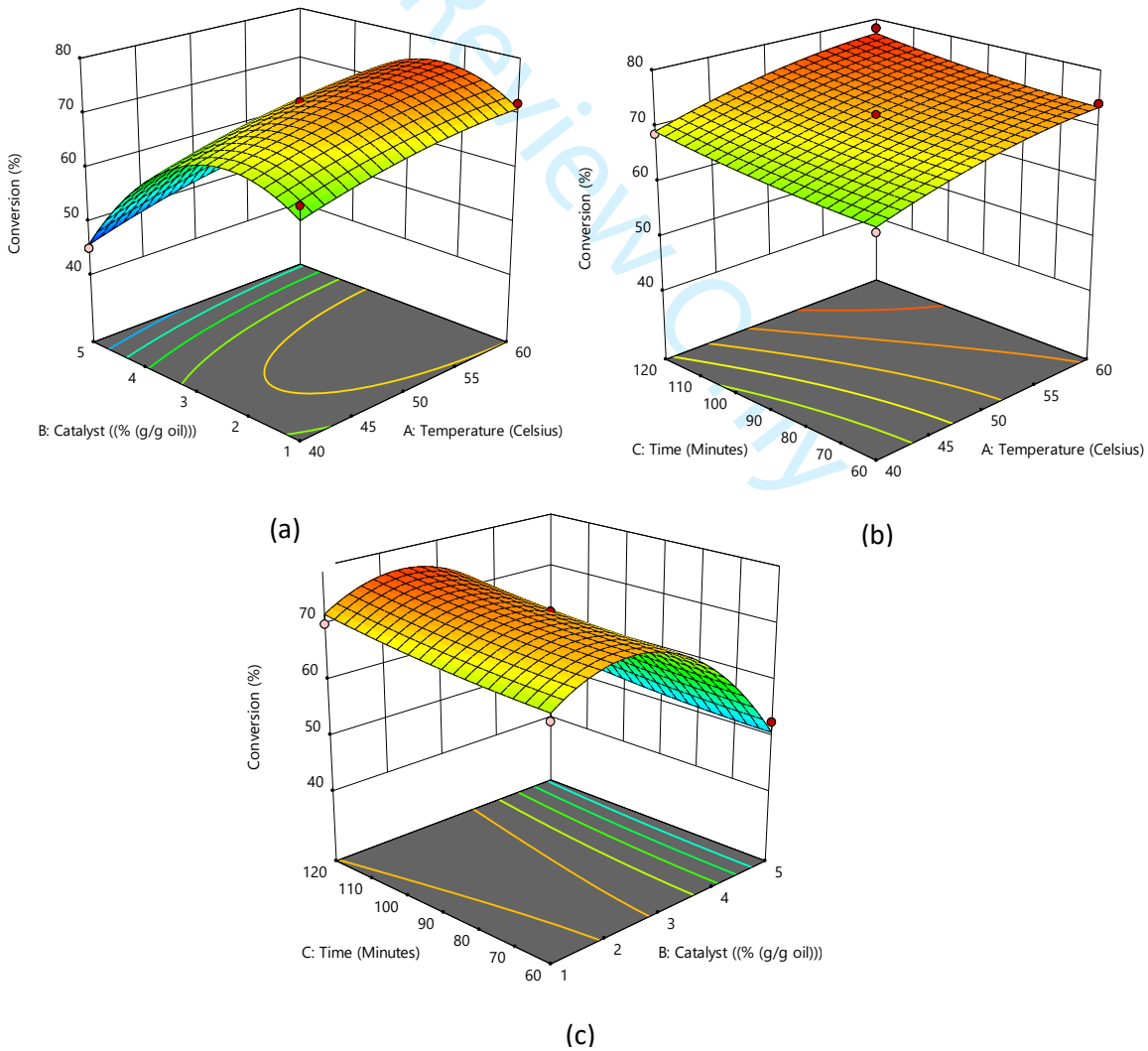


Figure 5. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Conversion. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50℃.

The significant variables affecting the FFA content and the FFA conversion were temperature and catalyst concentration as demonstrated in Figure 4 and 5, respectively. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to 60℃. Additionally, the increasing of catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, additional amount of catalyst employment did not result in the higher reaction conversion as well as the FFA removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

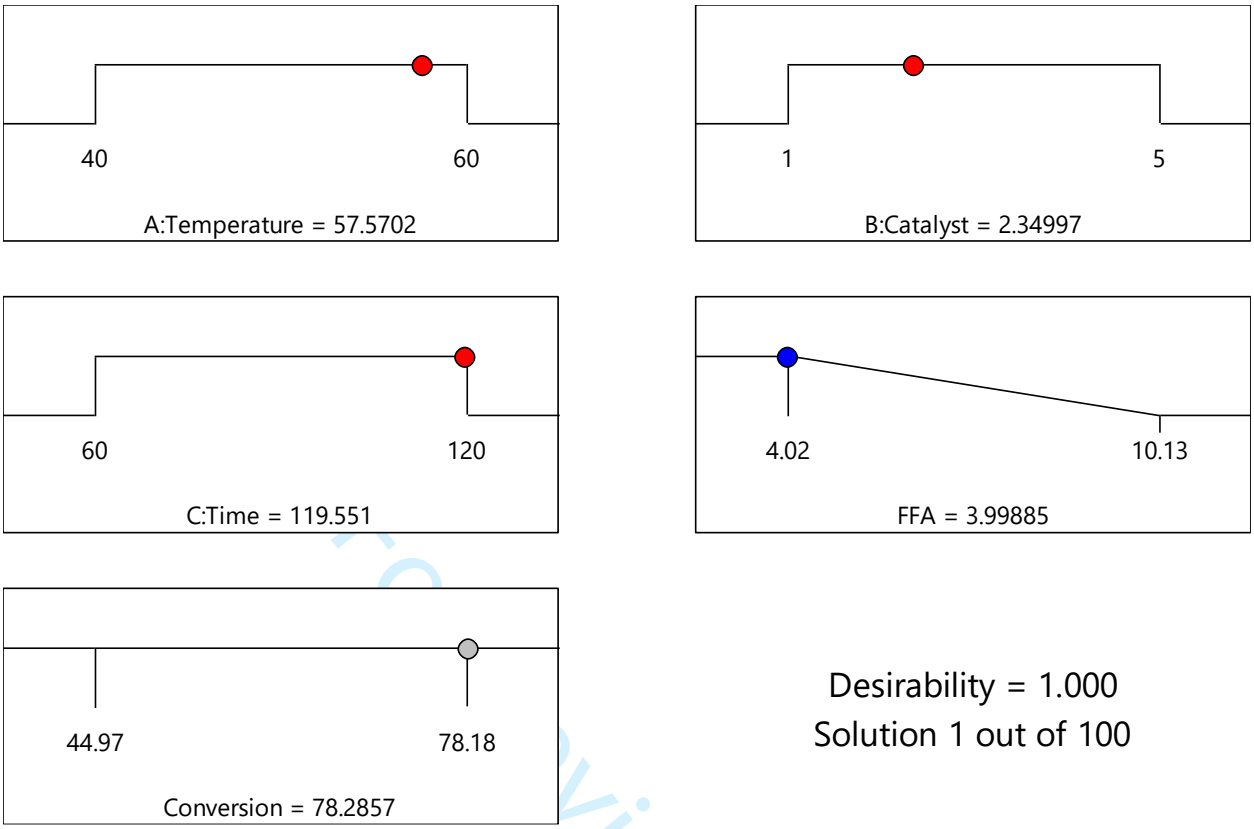


Figure 6. Optimization of FFA Conversion Using RSM (Quadratic Model)

In this work, Derringer Method was employed for the FFA conversion and FFA removal optimization in the esterification using sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as multi response problem based on Multi-criteria Decision Making. In this case, desirability approach is often employed as a vigorous instrument for optimization in multi response system. Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided undesired response. On the other hand, the value 1 indicates to the optimal condition of the parameter evaluated (Amdoun et al., 2018).

Based on the RSM simulation, it was revealed that the optimum conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 ^{o}C, catalyst concentration 1.98% g/g RNSO, and reaction time of 119.95 minutes. At this operation condition, the value of the desirability ramp was 1 (Figure 6). The result fitted the experimental

data and indicated the accuracy of the model. The similar method of optimization applying desirability function was also described by (Mourabet et al., 2017).

To predict the operation condition to achieve the FFA content of maximum 2%, extrapolation using RSM was carried out. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration, and reaction time were 58.97℃, 3%, and 194.9 minutes, respectively, whereas, molar ratio of oil to methanol was fixed at 1:30. The FFA conversion achieved was estimated 89.3%.

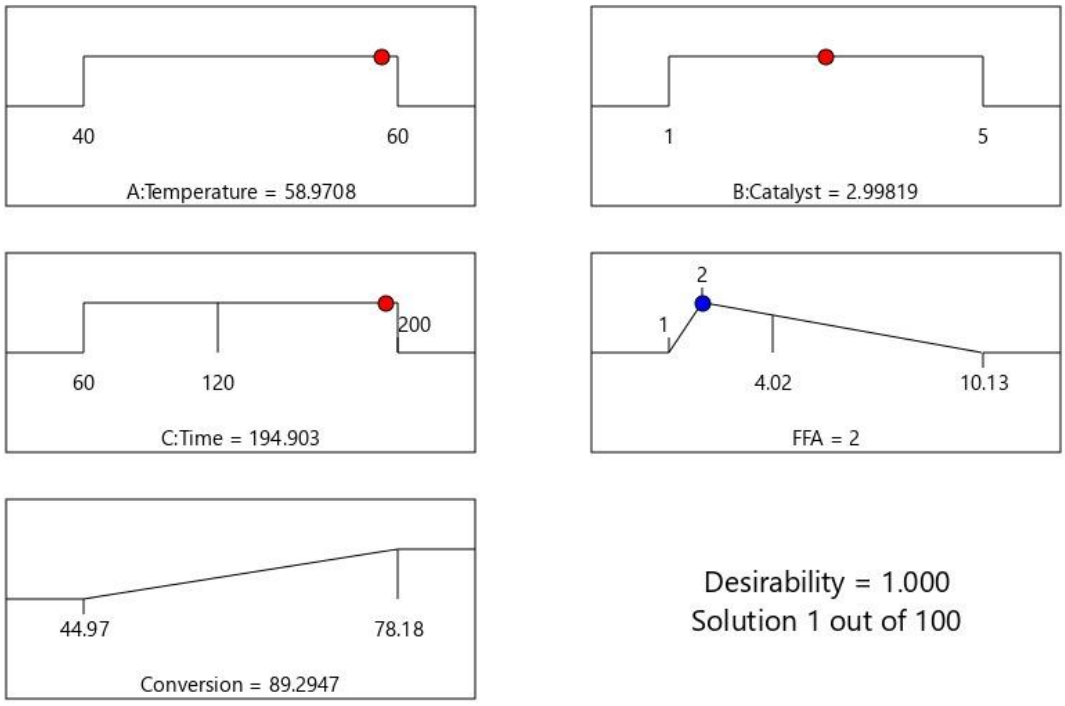


Figure 7. RSM Prediction of Operation Condition on the FFA Esterification Using Sulfuric Acid Catalyst to Decrease the FFA Content to 2%

The result has shown that RSM is simple and effective for process optimization. Furthermore, the combination of RSM and desirability function leads to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al., (2018). This study is significant to provide the optimum operation condition for reducing the FFA in

CNSO in order to fulfill the allowable level of FFA content before it is used as feedstock for biodiesel production via base catalyzed transesterification reaction.

CONCLUSION

The experimental work of FFA esterification in RNSO with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition at the reaction temperature of 60°C, reaction time of 120 minutes, molar ratio of RNSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. This value was not match with the maximum acceptable value of FFA content for alkaline catalyzed transesterification (2%). The RSM was performed to estimate the optimal operation condition for achieving the FFA content of 2%. The RSM model analysis demonstrated that the quadratic model was the most suitable model for optimization of this process in the future work. The RSM extrapolation predicted that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30.

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RESPONSE TO REVIEWER

Manuscript ID JST-2591-2021

Article Title:
Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) by Esterification Reaction: Experimental and Response Surface Methodology Analysis

Reviewer 1

No	Reviewer's Comment	Response
1	Regarding the model what you choose RSM, what for you fixed the goal of 2 % FFA Reduction	The explanation has been added in the introduction part: *The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction.*
2	What way you work differ from other published article in the same topic. I have seen more than enough.	The explanation has been added in the introduction part: *The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimization. The study on the FFA esterification in CNSO in the presence of sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimization has never been reported in the literature.*
3	What is the experimental setup whether you check the values using experimental setup and validated with references.	The reference has been added (Chai et al., 2014)
4	The Results should be discussed deeply to validate the data, but hardly not discussion	The more comprehensive discussion have been added into the Result and Discussion Part

Reviewer 2

No	Reviewer's Comment	Response
1	Title Suggest to revise the title	The title has been revised
2	Abstract The abstract contains all important information, however, it is too long for a journal paper, suggest to reduce according to the publisher guideline.	The abstract has been revised to make it more concise
3	Introduction 2nd sentence; term Thus far is not suitable, suggest to revise.	The word "thus far" has been replaced by "to date"
4	Page 3 Line 29/30; Double check the sentence; Mubarak Application of biodiesel/diesel fuel…	It has been revised
5	Materials and method Method The intro paragraph seems not relevant as it is a repetition information, suggest to remove.	The sentence has been removed.
6	Result and Discussion CNSO and RNSO Characterization Table 1: No explanation or discussion. The paragraph written is not complete.	A more comprehensive discussion has been added for Table 1.
7	Table 2: Define the NSO sample use	The explanation has been added:

	for this analysis. Why no comparison done between RNSO & CNSO?	*Fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process didn't significantly change the fatty acid composition.*
8	Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration 1st paragraph; double check the molar ratio of RNSO: methanol written in this paragraph. Different from the methods.	The molar ratio in the methods should be 1:30
9	Figure 1; Missing data for 5% at 50degC or is it overlapped?	It is overlapped
10	Pg 8 Line 4/5: "The FFA content of such the operation condition was 4.01%." Suggest to further explain the sentence.	The further explanation has been added *This value has not satisfied yet the maximum allowable FFA content of 2% for the transesterification reaction. Therefore, further observation was conducted at the different temperature and reaction time.*
11	Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time Paragraph 2 should mention which figure the explanation is about, double check the type error in this paragraph.	The figure explained (Figure 2) has been stated clearly and the type errors have been revised.
12	Response Surface Methodology	The explanation has been added

	(RSM) Analysis In the RSM, should justify why catalyst concentration, temperature, and reaction time are significant variable for the optimization.	*These variables were used for the optimization using RSM since they were the main parameters studied in experimental work*.
13	Pg 10; Line 7; "This full factorial design (Rodríguez-Ramírez et al., 2020)." Further clarify the sentence.	The type error has been revised
14	Pg 10; Line 50; The content of this paragraph is a repetition information in the earlier paragraph.	The sentence has been omitted
15	Table 5; no data for R2, Why? What is the normal R2 value for the esterification process?	The column for R^2 has been removed and the explanation was added. *In contrast, the values of actual R^2 were not presented in Table 5 since this table depicted the summary of the model test. The actual R^2 values were advanced investigated based on the values of predicted R^2.*
16	Figure 6 and 7 should further explain and discussed.	The discussion and reference have been added
17	Suggest to resize all the figures, using lots of spaces.	Several figures have been resized
18	Conclusion Conclusion is reflecting with the manuscript content.	The conclusion has been rewritten and developed

Reviewer 3

No	Reviewer's Comment	Response
1	Suggestion to rewrite the title	The title has been revised
2	Abstract Conclusion- its missing.	Abstract has been reformulated and correlated with the conclusion
3	Introduction Include study of other acid catalyst.	The study of other acid catalyst (homogeneous and heterogeneous) have been added
4	Methodology Line 34 page 4…what grade? Analytical?	It was analytical grade. The texts have been revised.
5	Line 47-50 page 4…rewrite	The paragraph has been developed and rewrite
6	Line 40 page 4 Method for characterization is missing.	
7	Line 45 page 5 how many runs?	The total experimental running was 7 experiments with different operation condition. Sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times.
8	Discussion Table 1&2-discuss	The discussion and additional references have been added
9	Table4 -Line Centre point? lack of fit? predicted r2?	The table has been set center point
10	Figure 4&5 No discussion, only results reported.	The discussion has been added
11	What is the novelty of this study?	The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimization. The study on the FFA esterification in CNSO in the presence of sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimization has never been reported in the literature.
12	What is the significance of this study?	This study is significant to provide the

		optimum operation condition for reducing the FFA in CNSO in order to fulfill the allowable level of FFA content before it is used as feedstock for biodiesel production via base catalyzed transesterification reaction.
13	Conclusion Rewrite	The conclusion has been rewritten

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Journal of Science and Technology - Decision on Manuscript ID JST-2591-2021.R1 (AA)

Journal of Science and Technology <onbehalfof@manuscriptcentral.com> Tue, Jul 6, 2021 at 7:13 AM
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06-Jul-2021

Dear Dr. Kusumaningtyas,

Manuscript ID JST-2591-2021.R1 entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis" which you submitted to the Journal of Science and Technology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter. I invite you to respond to the reviewer(s)' comments and revise your manuscript.

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Sincerely,
Chief Executive Editor, Journal of Science and Technology

Reviewer(s)' Comments to Author:

Reviewer: 3

Comments to the Corresponding Author
Abstract : add Conclusion

Journal of Science and Technology

Decision Letter (JST-2591-2021.R1)

From: executive_editor.pertanika@upm.edu.my

To: ratnadewi.kusumaningtyas@mail.unnes.ac.id

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Subject: Journal of Science and Technology - Decision on Manuscript ID JST-2591-2021.R1 (AA)

Body: 06-Jul-2021

Dear Dr. Kusumaningtyas,

Manuscript ID JST-2591-2021.R1 entitled "Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) by Esterification Reaction: Experimental and Response Surface Methodology Analysis" which you submitted to the Journal of Science and Technology, has been reviewed. The comments of the reviewer(s) are included at the bottom of this letter. I invite you to respond to the reviewer(s)' comments and revise your manuscript.

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Once again, thank you for submitting your manuscript to the Journal of Science and Technology and I look forward to receiving your revision.

Sincerely,
Chief Executive Editor, Journal of Science and Technology

Reviewer(s)' Comments to Author:

Reviewer: 3

Comments to the Corresponding Author
Abstract : add Conclusion

Date Sent: 06-Jul-2021

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Ratna Dewi Kusumaningtyas <ratnadewi.kusumaningtyas@mail.unnes.ac.id>

Journal of Science and Technology - Manuscript ID JST-2591-2021.R2

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09-Jul-2021

Dear Dr. Kusumaningtyas,

Your manuscript entitled "Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) using Response Surface Methodology Analysis" has been successfully submitted online and is presently being given full consideration for publication in the Journal of Science and Technology.

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Sincerely,
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Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) using Response Surface Methodology Analysis

Journal:	*Journal of Science and Technology*
Manuscript ID	JST-2591-2021.R2
Manuscript Type:	Regular Article
Scope of the Journal:	Biomass energy technology < Energy industry < APPLIED SCIENCES AND TECHNOLOGIES, Wood & non wood-based forest products < Resource-based industry < APPLIED SCIENCES AND TECHNOLOGIES, Oil < Resource-based industry < APPLIED SCIENCES AND TECHNOLOGIES, By-product utilisation < Agriculture engineering < ENGINEERING SCIENCES
Keywords:	biodiesel, esterification, sulfuric acid, RSM, FFA
Abstract:	Nyamplung seed (Calophyllum inophyllum L.) oil is a prospective non-edible vegetable oil as biodiesel feedstock, but it cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalyzed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18% and the FFA concentration was decreased to 4.01% at the temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable model for the FFA conversion optimization. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% can be obtained at the temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30. The results disclosed that RSM is an appropriate statistical method for optimizing the process variable in the esterification reaction to obtain the targeted value of FFA.

Running Title:

Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil

Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

Ratna Dewi Kusumaningtyas[1,*], Haniif Prasetiawan[1], Radenrara Dewi Artanti Putri[1], Bayu Triwibowo[1], Siti Choirunisa Furi Kurnita[1], Nanda Dwi Anggraeni[1], Harumi Veny[2], Fazlena Hamzah[2], Miradatul Najwa Muhd Rodhi[2]

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Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

Abstract

Nyamplung seed (*Calophyllum inophyllum L.*) oil is a prospective non-edible vegetable oil as biodiesel feedstock, but it cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalyzed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18% and the FFA concentration was decreased to 4.01% at the temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable model for the FFA conversion optimization. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% can be obtained at the temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30. The results disclosed that RSM is an appropriate statistical method for optimizing the process variable in the esterification reaction to obtain the targeted value of FFA.

Keywords: biodiesel; esterification; sulfuric acid; FFA; RSM; box-behnken; quadratic model

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. To date, fossil energy still dominates the energy supply all over the world (Ghasemian et al., 2020). However, the crude oil production in some countries shows a decline trend, which is not in balance

with the energy need. Besides, utilization of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, which contribute to the global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilization have led to the increasing interest on the renewable energy research. In the recent days, many countries in the world implement the policy to use fossil fuel and biofuel blending to ensure the energy sustainability and security. Biodiesel is a viable biofuel which can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is nontoxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristic, high flash point which ensure its safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Application of biodiesel/diesel fuel blends in diesel engine show an acceptable combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, to achieve complete conversion of one mol of triglycerides to alkyl esters; at least three moles of alcohol are required (Islam, 2014). The most common catalyst for biodiesel production is alkaline catalyst such as KOH, NaOH, or solid base catalyst. Transesterification process using alkaline catalyst is cheap and easy.

There are some potential biodiesel feedstocks in Indonesia, such as crude palm oil, jatropha oil, coconut oil, etc. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among the prospective local non edible oil in Indonesia for biodiesel production is nyamplung (*Calophyllum inophyllum L.*) seed oil (Musta et al., 2017; Silitonga et al., 2014). *Calophyllum inophyllum L* is extensively planted in Indonesia and the nyamplung seed oil can be purchased from the local farmers (Ong et al., 2019). Atabani & César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed satisfactory properties and good engine performance and emission in diesel machine.

However, crude nyamplung seed oil (CNSO) usually contains gum and high free fatty acid (FFA). The existence of high amount of FFA in feedstock is not desirable in alkaline catalyzed transesterification since it can react with the base catalyst, yielding the soap and diminish the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Generally, the maximum tolerable amount of FFA in base-catalyzed transesterification is 2%. Thus, a pre-treatment step to reduce the FFA content in nyamplung seed oil to maximum level of 2% prior to transesterification reaction is necessary. FFA removal in CNSO can be conducted through esterification reaction using methanol in the presence of acid catalyst. There are several types of acid catalyst for FFA esterification. They are categorized into the homogenous acid catalysts, for instance sulfuric acid, para-toluene sulfonic acid, phosphoric acid, and hydro, and HCl (Harun et al., 2018; Murad et al., 2018) and the heterogenous ones, such as Amberlyst 15, sulfated zirconia, niobic acid, zeolite, and tin (II) chloride (Banchero & Gozzelino, 2018; Dal Pozzo et al., 2019; Kusumaningtyas et al., 2014) Homogenous catalyst, particularly sulfuric acid, has been found as an efficient and economical catalyst for FFA esterification both at laboratory and industrial scales (Banani et al., 2015; Chai et al., 2014; Gebremariam & Marchetti, 2018). Therefore, sulfuric acid was selected as catalyst for the FFA removal via esterification reaction of CNSO oil in this work. The investigation included experimental work and the analysis using response surface methodology (RSM) to determine the optimal operation condition which yielded the targeted FFA final value of 2%. The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction. The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimization. The study on the FFA esterification in CNSO in the presence of sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimization has never been reported in the literature.

MATERIALS AND METHOD

Materials

Material used in this work were: crude nyamplung seed oil (CNSO), phosphoric acid (p.a., Merck), methanol (industrial grade, form local supplier), ethanol (analytical grade, from Merck), KOH (analytical grade, from Merck), oxalic acid (analytical grade, from Merck), sulfuric acid

(analytical grade, from Merck), distilled water (analytical grade, from local supplier), and phenolphthalein indicator (analytical grade, from Merck).

Methods

Nyampung Seed Oil Characterization

Prior to the esterification reaction, the crude nyamplung seed oil (CNSO) was first degummed using phosphoric acid to remove its gum content and resulted in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were then characterized to reveal their properties. The fatty acid composition was determined using Gas Chromatography-Mass Spectroscopy (GC-MS Perkin Elmer, GC Clarus 680, MS Clarus SQ 8T) with the similar method to our previous work (Kusumaningtyas et al., 2016). Density measurement was conducted using pycnometer (Taghizade, 2016). Viscosity determination was carried out using viscometer bath Stanhope-Seta KV6 tube 350 CFO. Acid value tests was accomplished based on the AOCS acid-base titration method (Banchero & Gozzelino, 2018).

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using hot plate at 70℃. Sulfuric acid with the concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm distilled water (40-50℃ in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated entirely. The two layers were formed. The top and bottom layers were refined nyamplung seed oil (RNSO) and gum, respectively. To remove the water content, the RNSO were then heated using oven at 105℃ until it reached the constant weight.

FFA Removal

The FFA removal was conducted via esterification reaction with methanol employing sulfuric acid. RNSO and methanol were weighed to obtain the molar ratio of RNSO and methanol of 1:30. RNSO was introduced into the three necks flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at the identical temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into

the reactor. The reaction temperatures were varied at 40℃, 50℃, and 60℃. Sulfuric acid catalyst was afterward added at a certain concentration (1%, 3%, 5%, 7% w/w RNSO). The reaction was carried out for 120 minutes. A constant mixing using magnetic stirrer with the speed of 1000 rpm was performed to certify the homogeneous reaction. The total experimental running was 7 experiments with different operation condition. Sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples were calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

Response Surface Methodology

Response Surface Methodology using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the box-behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic were evaluated to determine the most appropriate model for optimization. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of crude nyamplung seed oil (CNSO) and refined nyamplung seed oil (RNSO) which has undergone degumming process were demonstrated in Table 1. Degumming process aims for reducing the gum content. Besides, degumming has also brought about a better characteristic of the oil feedstock. It can be observed in Table 1, the density viscosity, acid number, and acidity of the RNSO were lower than CNSO. The decreasing value of density happened due to the losses of some heavy compound such as gum. The degumming process also caused a lighter color of the oil. It was due to the removal of the compounds which significantly affected the oil color (Lamas et al., 2016). Degumming process has shown a better characteristic of the oil feedstock, leading to an effective transesterification reaction and a higher quality of biodiesel product.

Table 1

Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

Composition of fatty acid in CNSO was determined using GC-MS and the result was exhibited in Table 2. Based on this composition, the molecular weight of CNSO can be calculated. It was found that CNSO molecular weight was 869.74 g/mol and the most dominant fatty acid in CNSO were oleic acid and linoleic acids. It is in a good agreement with the fatty acid composition found by Aparamarta et al. (2020). Fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process didn't significantly change the fatty acid composition.

Table 2

Crude Nyamplung Seed Oil (CNSO) Fatty Acid Composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55
Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

FFA (free fatty acid) removal was conducted via esterification reaction of RNSO and methanol in the presence of sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied

at 1%, 3%, 5%, dan 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40℃, 50℃, and 60℃. Encinar et al. (2021) suggested the sulfuric acid catalyst concentration of 0.5 – 2% for the feedstock with FFA content of 10.7%. The higher sulfuric catalyst concentration can be employed for the higher acidic vegetable oils. The molar ratio of oil to methanol referred to Chai et al. (2014) that recommended the molar ratio of oil to methanol in the range of 1:20 to 1:60. Specifically, Marchetti & Errazu (2008) proposed the molar ratio of 1:30 as the optimal condition. On the other hand, the reaction temperature ratio was adjusted to the boiling point of the methanol. The reaction was run for 120 minutes as suggested by Chai et al. (2014). The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

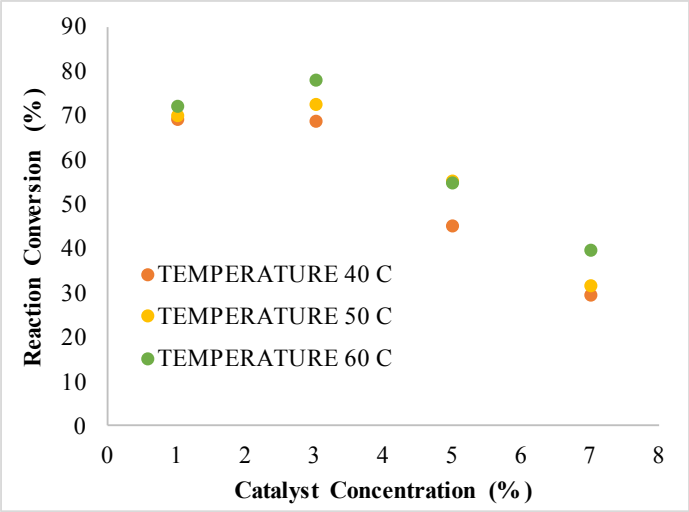


Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of RNSO to Methanol of 1:30

It can be observed in Figure 1, reaction conversion increased at the catalyst concentration 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in the higher possibility of the reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the higher reaction concentration (5% to 7%), the apparent reaction conversion declined since the excessive amount of catalyst could provoke the side reaction and reduced the FFA conversion (Widiarti et al., 2017). The excessive employment of catalyst will correspondingly bring about the difficulty and higher cost in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the

temperature of 60℃ with the reaction time of 120 minutes. The FFA content of such the operation condition was 4.01%. This value has not satisfied yet the maximum allowable FFA content of 2% for the transesterification reaction. Therefore, further observation was conducted at the different temperature and reaction time.

3. 2. Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that, the higher reaction temperature, the higher removal of FFA occurred. This phenomenon was due to the fact that the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increasing of the reaction temperature raised the FFA conversion. This fact was also in agreement with the Arrhenius Law which states that the reaction rate is equivalent with the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. In accordance with the Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature risen.

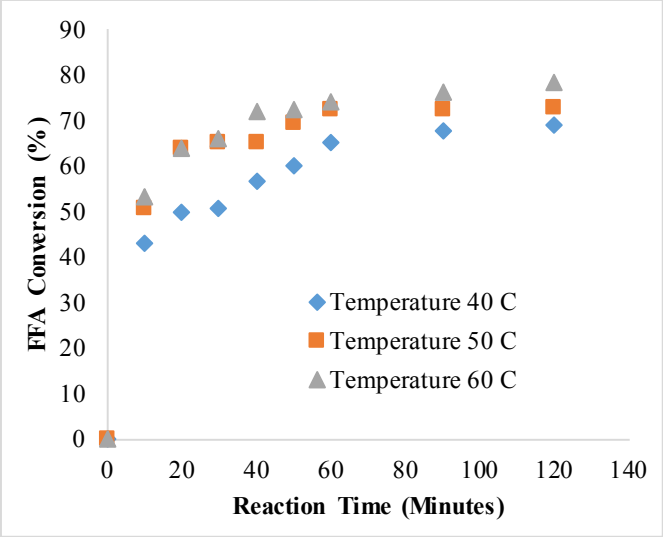


Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of RNSO and Methanol of 1:30

As shown in Figure 2, it was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 – 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. Based on catalyst concentration

alteration (Figure 1) as well as the temperature and reaction time variation (Figure 2), it was revealed that the best conversion was achieved at the catalyst concentration of 3%, molar ratio of RNSO to methanol of 1:30, reaction temperature of 60℃, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal in kapok randu seed oil using methanol reactant and sulfuric acid catalyst was 60℃ and reaction time of 120 minutes (Kusumaningtyas et al., 2019). Among the promising way to enhance the reaction conversion is by increasing the reaction temperature to 65℃ and applying higher molar ratio of the reactants as accomplished by Chai et al. (2014). In this work, the lowest FFA content obtained among all the experiments conducted was 4.01%. It didn't match with the standard limitation of FFA content for base catalyzed transesterification (2%). Therefore, response surface methodology optimization was then carried out to predict the optimum operation condition of the esterification reaction which can yield the 2% FFA content of RNSO.

Response Surface Methodology (RSM) Analysis

The result of the FFA removal was under the targeted value of FFA content (maximum 2%). Thus, optimization using response surface methodology (RSM) will be beneficial for designing the operation condition to achieve the targeted conversion. RSM is a set of mathematical and statistical tools which can be used for developing empirical model which correlate the reaction conversion or the yield of product with the significant process parameters (Veljković et al., 2019). Application of this tool has been found to be valuable to reduce the experimental cost (J. Liu et al., 2018). However, there are several models provided for the optimization using RSM. Hence, the suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. The similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this study, the best polynomial model will be useful to be applied in the future work for designing the experiment condition and improving the conversion of the reaction. To select the model, combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification in RNSO using sulfuric acid catalyst were investigated. These variables were used for the optimization using RSM since they were the

main parameters studied in experimental work. Experiments with the different combination of the three variables were conducted and calculated statistically using experimental design which was based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial (Rodríguez-Ramírez et al., 2020). This full factorial design is the most commonly applied in RSM optimization (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Tabel 3
Experimental Design Using Box-Behnken Methodology (BBD) which Equipped with the Experimental Data and Predictive Result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25
2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The four polynomial models, namely linear, interactive (2FI), quadratic, and cubic were used to predict the response variable to the experimental data. Two types of tests, i.e., sequential model sum of squares and model summary were used as the basic for the polynomial model

determination which is suitable for optimizing the FFA conversion. The result is shown in Table 4 and 5, respectively.

Table 4

Sequential Model Sum of Squares Test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Qubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						
Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Qubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Tabel 5

Model Summary Test

Component	Std. Dev	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content					
Linear	**0.0250**	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	0.2604	-0.8490	-	0.9989
Quadratik	**0.0221**	**0.9172**	**-**	**Suggested**	**0.0221**
Qubic	**-**	-	-	Aliased	**-**
Model summary of FFA Conversion					
Linear	**0.0249**	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	**0.9171**	**-**	**Suggested**	**0.0222**
Qubic	**-**	-	-	Aliased	**-**

Based on the result shown in Table 4 and 5, it was acquired that the quadratic model was justified as the most suitable model for optimizing the FFA content and conversion in the esterification using sulfuric acid catalyst. The basis of the selection of the quadratic model was the lowest p-value, the highest value of adjusted R^2, and the highest value of predicted R^2. Tabel 4 reveals that the quadratic model provided the lowest p-value. Table 5 shows that the highest value of adjusted R^2 was provided by the quadratic model. Meanwhile, the predicted R^2 for the quadratic model didn't appear in Table 5 since the value was precisely closed to 1. In contrast, the values of actual R^2 were not presented in Table 5 since this table depicted the summary of the model test. The actual R^2 values were advanced investigated based on the values of predicted R^2. Based on the values of the p-value, adjusted R^2, and predicted R^2 attained, the quadratic model was found as the most suitable model and further analyzed using ANOVA. This finding is in line the result analysis of Maran & Priya (2015), which suggested that quadratic model was the most appropriate model.

The empirical model which was expressed using quadratic model with the interaction obtained from the experimental data based on the RSM was modified into polynomial equation. The final equation for FFA content and FFA conversion optimization are presented in the Eq. 1 dan Eq. 2, respectively.

FFA Content (%) = 16.5 – 0.306 A – 2.2 B + 0.014 C – 0.0059 AB – 0.000042 AC + 0.0005 BC + 0.0026 A^2 + 0.54 B^2 – 0.00014 C^2 (1)

FFA Conversion (%) = 10.63 + 1.66 A + 11.91B – 0.081 C + 0.032 AB + 0.00026 AC + 0.0026 BC – 0.014 A^2 – 2.94 B^2 + 0.00075 C^2 (2)

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6

ANOVA Regression Model to Predict the FFA Conversion Using Sulfuric Acid Catalyst

Source	*Sum of square*	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	

X_{23}	0.0992	1	0.0992	0.0120	0.9197
X_1^2	4.37	1	4.37	0.5278	0.5201
X_2^2	315.17	1	315.17	38.08	0.0086
X_3^2	1.04	1	1.04	0.1258	0.7463
Residual	24.83	3	8.28		
Cor Total	1197.58	12			
Adeq prec	12.46				

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential which could cause the model unsuccessful to predict the value of response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision is the measure of the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. Ratio of 12.46 resulted in this work denoted that the inputted signal was appropriate.

Validation of the model capability in predicting is necessary to ensure the accuracy of model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the calculation using the model was close to the experimental data. It was indicated by the point of the response values of prediction and experimental just about the 45^o line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

The model suitability was further diagnosed by constructing a plot between the externally studied residuals with the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error which could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the result of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimization in the FFA esterification using sulfuric acid catalyst. The graphical illustration, termed response surface, is

frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).

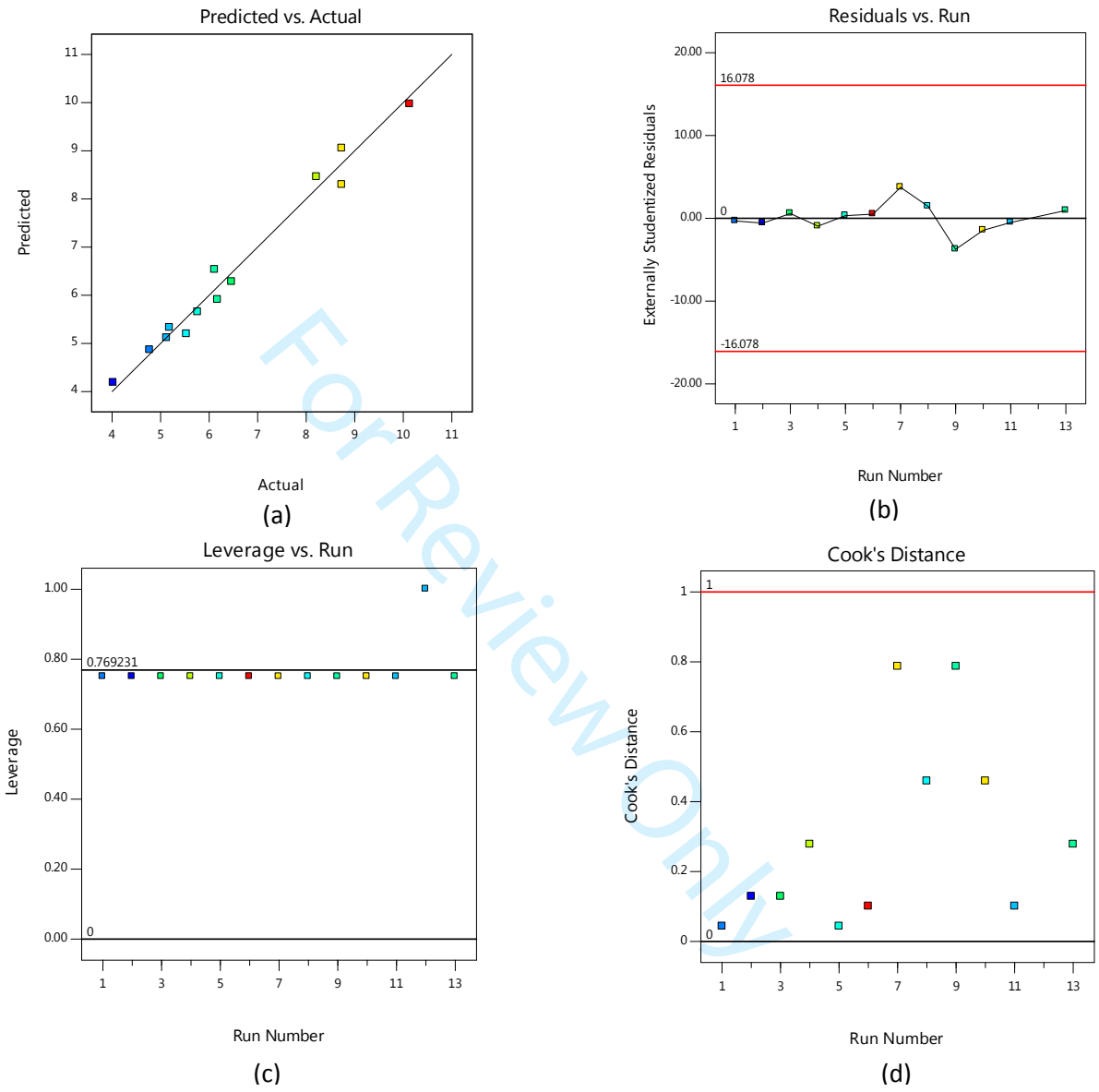


Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

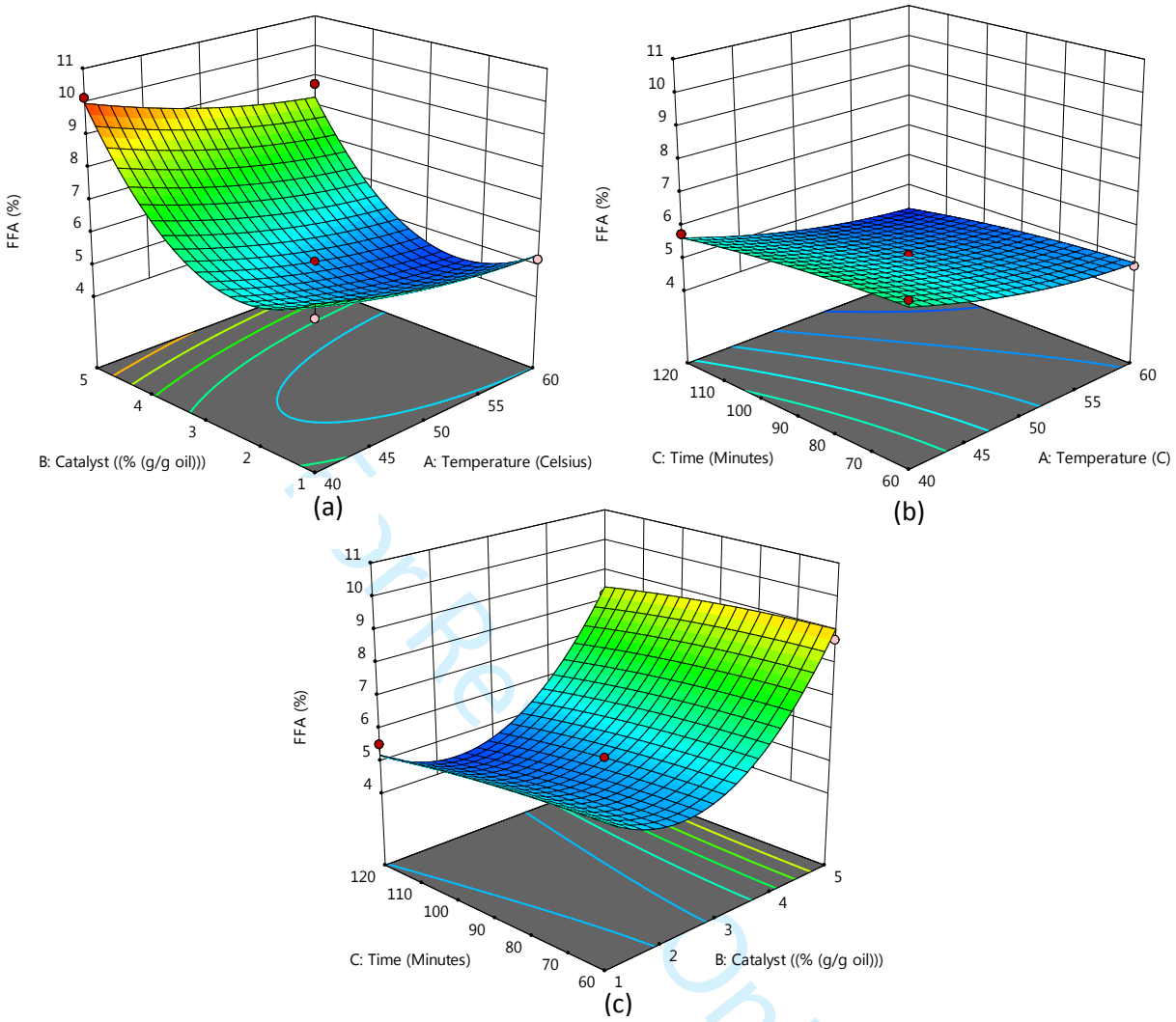
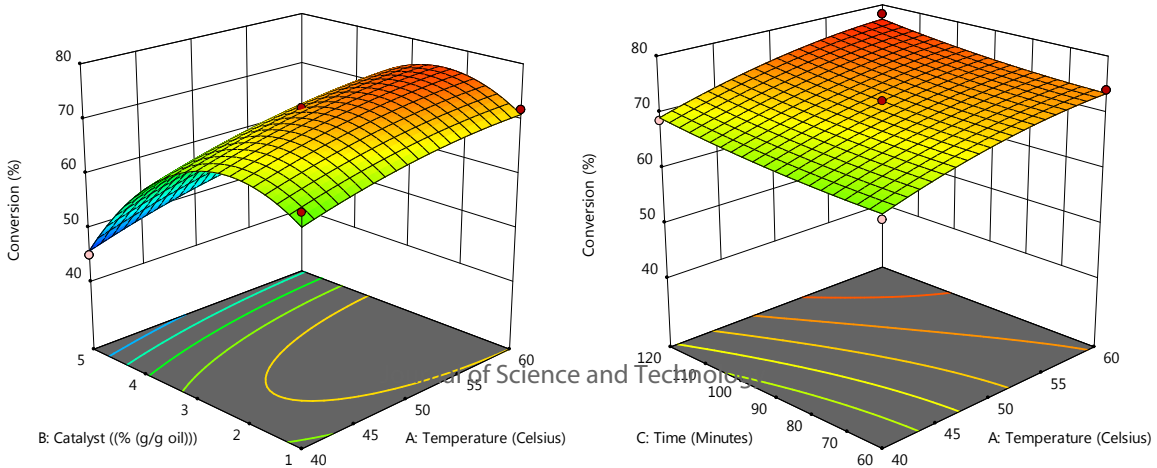


Figure 4. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Content. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50℃.



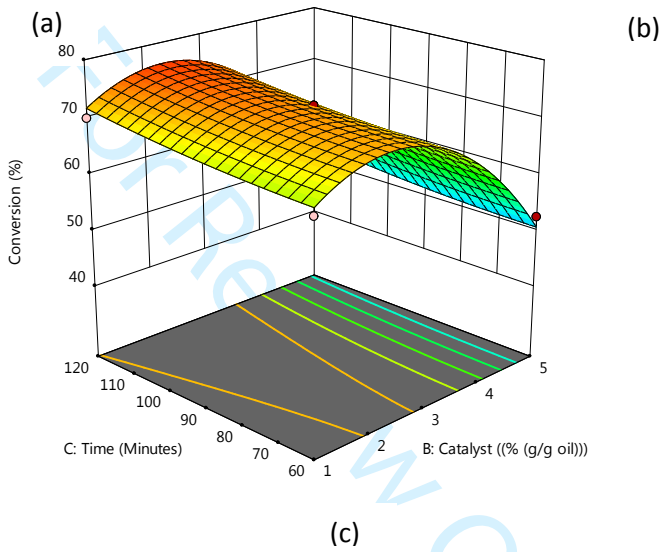


Figure 5. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Conversion. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50℃.

The significant variables affecting the FFA content and the FFA conversion were temperature and catalyst concentration as demonstrated in Figure 4 and 5, respectively. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to 60℃. Additionally, the increasing of catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, additional amount of catalyst employment did not result in the higher reaction conversion as well as the FFA removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

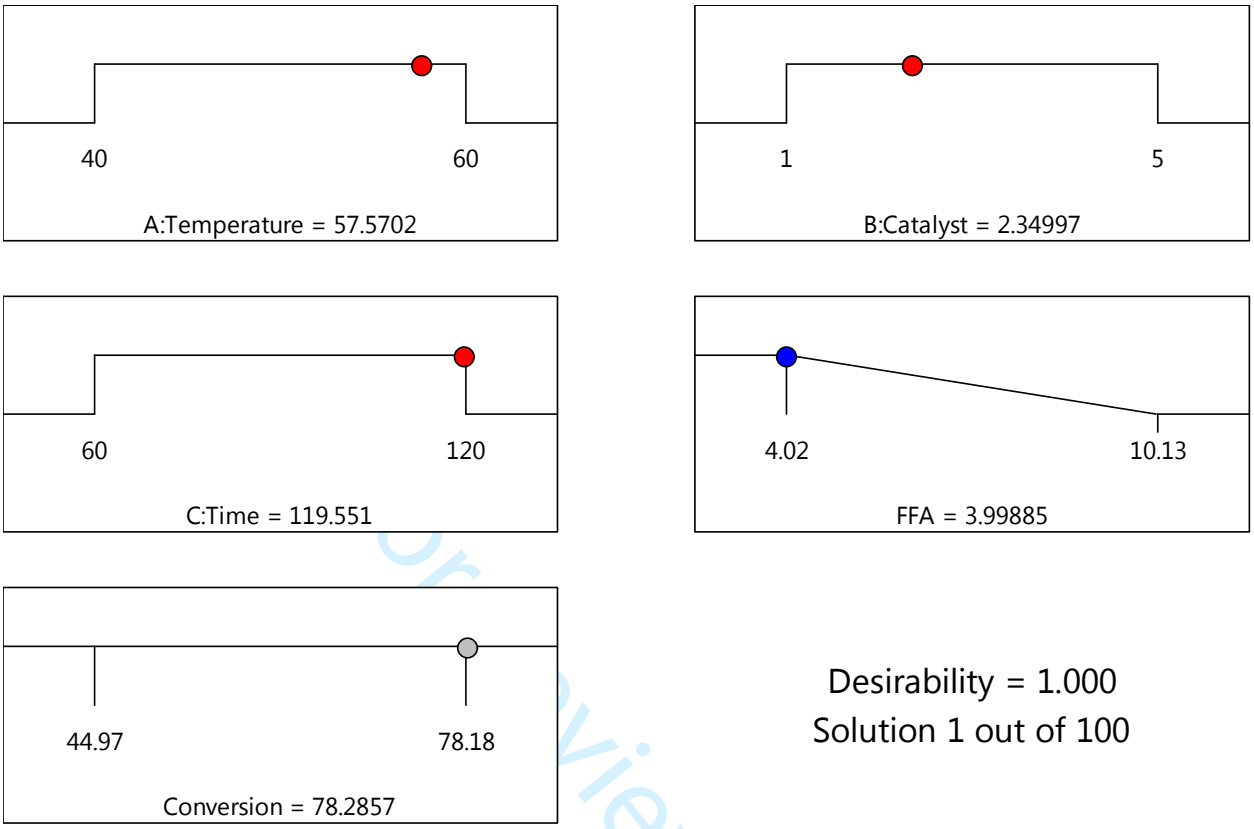


Figure 6. Optimization of FFA Conversion Using RSM (Quadratic Model)

In this work, Derringer Method was employed for the FFA conversion and FFA removal optimization in the esterification using sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as multi response problem based on Multi-criteria Decision Making. In this case, desirability approach is often employed as a vigorous instrument for optimization in multi response system. Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided undesired response. On the other hand, the value 1 indicates to the optimal condition of the parameter evaluated (Amdoun et al., 2018).

Based on the RSM simulation, it was revealed that the optimum conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 ^{o}C, catalyst concentration 1.98% g/g RNSO, and reaction time of 119.95 minutes. At this operation

condition, the value of the desirability ramp was 1 (Figure 6). The result fitted the experimental data and indicated the accuracy of the model. The similar method of optimization applying desirability function was also described by (Mourabet et al., 2017).

To predict the operation condition to achieve the FFA content of maximum 2%, extrapolation using RSM was carried out. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration, and reaction time were 58.97℃, 3%, and 194.9 minutes, respectively, whereas, molar ratio of oil to methanol was fixed at 1:30. The FFA conversion achieved was estimated 89.3%.

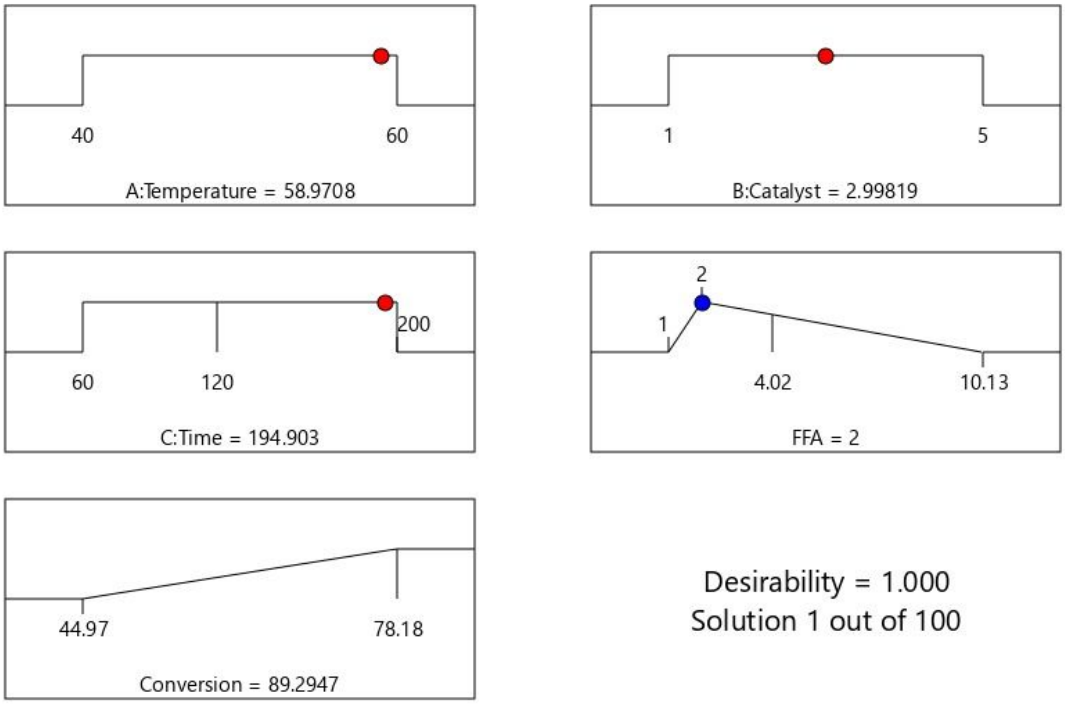


Figure 7. RSM Prediction of Operation Condition on the FFA Esterification Using Sulfuric Acid Catalyst to Decrease the FFA Content to 2%

The result has shown that RSM is simple and effective for process optimization. Furthermore, the combination of RSM and desirability function leads to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al., (2018). This study is significant to provide the optimum operation condition for reducing the FFA in CNSO in

order to fulfill the allowable level of FFA content before it is used as feedstock for biodiesel production via base catalyzed transesterification reaction.

CONCLUSION

The experimental work of FFA esterification in RNSO with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition at the reaction temperature of 60℃, reaction time of 120 minutes, molar ratio of RNSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. This value was not match with the maximum acceptable value of FFA content for alkaline catalyzed transesterification (2%). The RSM was performed to estimate the optimal operation condition for achieving the FFA content of 2%. The RSM model analysis demonstrated that the quadratic model was the most suitable model for optimization of this process in the future work. The RSM extrapolation predicted that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30.

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The funding resource from the Research and Community Service Institute (LPPM) of Universitas Negeri Semarang through Collaborative Research Scheme (UNNES-UiTM Matching Grant) with Contract Number of 101.23.4/UN37/PPK.3.1/2020 is highly acknowledged.

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Article Title:
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Revised Title:
Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

Reviewer 3

No	Reviewer's Comment	Response
1	Abstract: add Conclusion	The conclusion has been added to the abstract: The results disclosed that RSM is an appropriate statistical method for optimizing the process variable in the esterification reaction to obtain the targeted value of FFA.

RESPONSE TO REVIEWER

Manuscript ID JST-2591-2021

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Revised Title:
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Reviewer 3

No	Reviewer's Comment	Response
1	Abstract: add Conclusion	The conclusion has been added to the abstract: The results disclosed that RSM is an appropriate statistical method for optimizing the process variable in the esterification reaction to obtain the targeted value of FFA.

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☐ Debit Rek./*Debit Acc. No.* - 0246582443

Mata Uang/*Currency* : ☐ IDR ☑ USD ☐

Jumlah Dana yang dikirim/*Amount Transfer* :

Jumlah/*Amount*	Kurs/*Rate*	Nilai/*Total Amount*
250	14.685	3.671.25

Biaya/*Charge*	Valas/*Amount in Foreign Exchange*	Kurs/*Rate*	Nilai/*Total Amount*
Komisi/*Commission* OBIC 25			367.125
Pengiriman/*Handling* Basic 2.38			35.00
Bank Koresponden/*Correspondent Bank*			
Jumlah Biaya/*Amount Charge*			
Total yang dibayarkan/*Total Amount*	277.38		4.073.375

Terbilang/*Amount in Words* :

Empat juta tujuh puluh tiga ribu tiga ratus tujuh puluh lima rupiah

Tujuan Transaksi (*Transaction Purpose*) PERTAMINA PROCESSING FEE JST-2591-2021-R2

Berita (*Message*) C125161/T07039243821)

Biaya dari Bank koresponden dibebankan ke rekening/ *Correspondent bank charges are for account of* :

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Saya mengetahui ketentuan-ketentuan syarat-syarat yang tercantum pada halaman belakang formulir ini dan menyetujuinya/ *I have read and unconditionally accept all the terms and conditions on the reverse form.*

Pejabat Bank/*Bank Officer*

Pemohon/*Applicant*

Lembar 1 & 2 : untuk Bank, Lembar 3 : untuk Nasabah

PT. BANK NEGARA INDONESIA (Persero), Tbk
CABANG : SEMARANG

IBOC - Maintenance (S10)

Teller ID : 88593
Date : 22/07/2021
Time : 10:52:33

Sender's Reference:
:20:S10SMG00184021
Bank Operation Code:
:23B:CRED
Value Date/Currency/Interbank Settled Amount:
:32A:210722USD250,
Ordering Customer:
:50K:/0246582443
RATNA DEWI KUSUMANINGTYAS
SEMARANG INDONESIA
08174111880
Ordering Institution:
:52A:BNINIDJAXXX
Account With Institution:
:57D:CIMB BANK BERHAD
PETALING MALAYSIA
SWIFT CODE CIBBMYKL
Beneficiary Customer:
:59:/8002151963
KIRA KIRA AM UPM
SERDANG SELANGOR MALAYSIA
Remittance Intormation:
:70:PERTANIKA PROCESSING FEE
JST 2591 2021 R2 C125161
T070392343821
Details Of Charges:
:71A:OUR

PT. BANK NEGARA INDONESIA (PERSERO) KANTOR CABANG UNNES SEMARANG

UNNES
UNIVERSITAS NEGERI SEMARANG

Ratna Dewi Kusumaningtyas <ratnadewi.kusumaningtyas@mail.unnes.ac.id>

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Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil

Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

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ABSTRACT

Nyamplung seed (*Calophyllum inophyllum L.*) oil is a prospective non-edible vegetable oil as biodiesel feedstock, but it cannot be directly used in the alkaline catalyzed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalyzed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18% and the FFA concentration was decreased to 4.01% at the temperature of 60℃ and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable model for the FFA conversion optimization. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09℃, 1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% can be obtained at the temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30. The results disclosed that RSM is an appropriate statistical method for optimizing the process variable in the esterification reaction to obtain the targeted value of FFA.

Keywords: Biodiesel; Box-Behnken; esterification; FFA; quadratic model; RSM; sulfuric acid

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. To date, fossil energy still dominates the energy supply all over the world (Ghasemian et al., 2020). However, the crude oil production in some countries shows a decline trend, which is not in balance with the energy need. Besides, utilization of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, which contribute to the global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilization have led to the increasing interest on the renewable energy research. In the recent days, many countries in the world implement the policy to use fossil fuel and biofuel blending to ensure the energy sustainability and security. Biodiesel is a viable biofuel which can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is nontoxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristic, high flash point which ensure its safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Application of biodiesel/diesel fuel blends in diesel engine show an acceptable combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, to achieve complete conversion of one mol of triglycerides to alkyl esters; at least three moles of alcohol are required (Islam, 2014). The most common catalyst for biodiesel production is alkaline catalyst such as KOH, NaOH, or solid base catalyst. Transesterification process using alkaline catalyst is cheap and easy.

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There are some potential biodiesel feedstocks in Indonesia, such as crude palm oil, jatropha oil, and coconut oil. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among the prospective local non edible oil in Indonesia for biodiesel production is nyamplung (*Calophyllum inophyllum L.*) seed oil (Musta et al., 2017; Silitonga et al., 2014). *Calophyllum inophyllum L* is extensively planted in Indonesia and the nyamplung seed oil can be purchased

from the local farmers (Ong et al., 2019). Atabani and César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed satisfactory properties and good engine performance and emission in diesel machine.

However, crude nyamplung seed oil (CNSO) usually contains gum and high free fatty acid (FFA). The existence of high amount of FFA in feedstock is not desirable in alkaline catalyzed transesterification since it can react with the base catalyst, yielding the soap and diminish the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Generally, the maximum tolerable amount of FFA in base-catalyzed transesterification is 2%. Thus, a pre-treatment step to reduce the FFA content in nyamplung seed oil to maximum level of 2% prior to transesterification reaction is necessary. FFA removal in CNSO can be conducted through esterification reaction using methanol in the presence of acid catalyst. There are several types of acid catalyst for FFA esterification. They are categorized into the homogenous acid catalysts, for instance sulfuric acid, para-toluene sulfonic acid, phosphoric acid, and hydro, and HCl (Harun et al., 2018; Murad et al., 2018) and the heterogenous ones, such as Amberlyst 15, sulfated zirconia, niobic acid, zeolite, and tin (II) chloride (Banchero & Gozzelino, 2018; Dal Pozzo et al., 2019; Kusumaningtyas et al., 2014) Homogenous catalyst, particularly sulfuric acid, has been found as an efficient and economical catalyst for FFA esterification both at laboratory and industrial scales (Banani et al., 2015; Chai et al., 2014; Gebremariam & Marchetti, 2018). Therefore, sulfuric acid was selected as catalyst for the FFA removal via esterification reaction of CNSO oil in this work. The investigation included experimental work and the analysis using response surface methodology (RSM) to determine the optimal operation condition which yielded the targeted FFA final value of 2%. The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction. The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimization. The study on the FFA esterification in CNSO in the presence of sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimization has never been reported in the literature.

MATERIALS AND METHODS

Materials

Material used in this work were: crude nyamplung seed oil (CNSO), phosphoric acid (p.a., Merck), methanol (industrial grade, form local supplier), ethanol (analytical grade, from Merck), KOH (analytical grade, from Merck), oxalic acid (analytical grade, from Merck), sulfuric acid (analytical grade, from Merck), distilled water (analytical grade, from local supplier), and phenolphthalein indicator (analytical grade, from Merck).

Nyampung Seed Oil Characterization

Prior to the esterification reaction, the crude nyamplung seed oil (CNSO) was first degummed using phosphoric acid to remove its gum content and resulted in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were then characterized to reveal their properties. The fatty acid composition was determined using Gas Chromatography-Mass Spectroscopy (GC-MS Perkin Elmer, GC Clarus 680, MS Clarus SQ 8T) with the similar method to our previous work (Kusumaningtyas et al., 2016). Density measurement was conducted using pycnometer (Taghizade, 2016). Viscosity determination was carried out using viscometer bath Stanhope-Seta KV6 tube 350 CFO. Acid value tests was accomplished based on the AOCS acid-base titration method (Banchero & Gozzelino, 2018).

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using hot plate at 70℃. Sulfuric acid with the concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm distilled water (40-50℃ in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated entirely. The two layers were formed. The top and bottom layers were refined nyamplung seed oil (RNSO) and gum, respectively. To remove the water content, the RNSO were then heated using oven at 105℃ until it reached the constant weight.

FFA Removal

The FFA removal was conducted via esterification reaction with methanol employing sulfuric acid. RNSO and methanol were weighed to obtain the molar ratio of RNSO and methanol of 1:30.

RNSO was introduced into the three necks flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at the identical temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into the reactor. The reaction temperatures were varied at 40℃, 50℃, and 60℃. Sulfuric acid catalyst was afterward added at a certain concentration (1%, 3%, 5%, 7% w/w RNSO). The reaction was carried out for 120 minutes. A constant mixing using magnetic stirrer with the speed of 1000 rpm was performed to certify the homogeneous reaction. The total experimental running was 7 experiments with different operation condition. Sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples were calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

Response Surface Methodology

Response Surface Methodology using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the Box-Behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic were evaluated to determine the most appropriate model for optimization. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of crude nyamplung seed oil (CNSO) and refined nyamplung seed oil (RNSO) which has undergone degumming process were demonstrated in Table 1. Degumming process aims for reducing the gum content. Besides, degumming has also brought about a better characteristic of the oil feedstock. It can be observed in Table 1, the density viscosity, acid number, and acidity of the RNSO were lower than CNSO. The decreasing value of density happened due to the losses of some heavy compound such as gum. The degumming process also caused a lighter color of the oil. It was due to the removal of the compounds which significantly affected the oil color (Lamas et al., 2016). Degumming process has shown a better characteristic of the oil

feedstock, leading to an effective transesterification reaction and a higher quality of biodiesel product.

Table 1

Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

Composition of fatty acid in CNSO was determined using GC-MS and the result was exhibited in Table 2. Based on this composition, the molecular weight of CNSO can be calculated. It was found that CNSO molecular weight was 869.74 g/mol and the most dominant fatty acid in CNSO were oleic acid and linoleic acids. It is in a good agreement with the fatty acid composition found by Aparamarta et al. (2020). Fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process didn't significantly change the fatty acid composition.

Table 2

Crude Nyamplung Seed Oil (CNSO) Fatty Acid Composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55
Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

free fatty acid (FFA) removal was conducted via esterification reaction of RNSO and methanol in the presence of sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied at 1%, 3%, 5%, dan 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40℃, 50℃, and 60℃. Encinar et al. (2021) suggested the sulfuric acid catalyst concentration of 0.5 – 2% for the feedstock with FFA content of 10.7%. The higher sulfuric catalyst concentration can be employed for the higher acidic vegetable oils. The molar ratio of oil to methanol referred to Chai et al. (2014) that recommended the molar ratio of oil to methanol in the range of 1:20 to 1:60. Specifically, Marchetti & Errazu (2008) proposed the molar ratio of 1:30 as the optimal condition. On the other hand, the reaction temperature ratio was adjusted to the boiling point of the methanol. The reaction was run for 120 minutes as suggested by Chai et al. (2014). The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

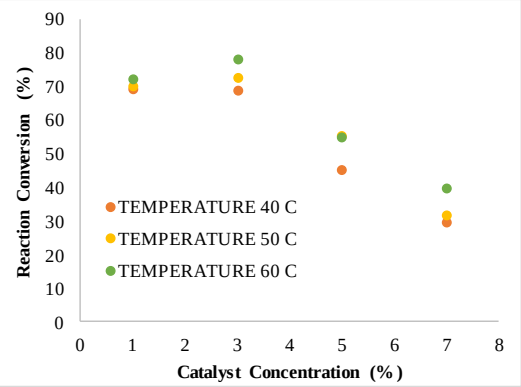

Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of RNSO to Methanol of 1:30

It can be observed in Figure 1, reaction conversion increased at the catalyst concentration 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in the higher possibility of the reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the higher reaction concentration (5% to 7%), the apparent reaction conversion declined since the excessive amount of catalyst could provoke the side reaction and reduced the FFA conversion (Widiarti et

al., 2017). The excessive employment of catalyst will correspondingly bring about the difficulty and higher cost in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the temperature of 60℃ with the reaction time of 120 minutes. The FFA content of such the operation condition was 4.01%. This value has not satisfied yet the maximum allowable FFA content of 2% for the transesterification reaction. Therefore, further observation was conducted at the different temperature and reaction time.

Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that, the higher reaction temperature, the higher removal of FFA occurred. This phenomenon was due to the fact that the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increasing of the reaction temperature raised the FFA conversion. This fact was also in agreement with the Arrhenius Law which states that the reaction rate is equivalent with the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. In accordance with the Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature risen.

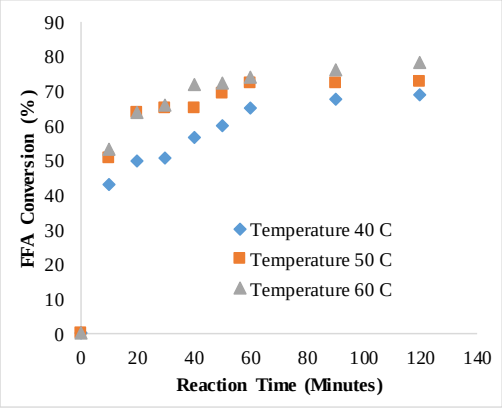

Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of RNSO and Methanol of 1:30

As shown in Figure 2, it was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 – 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. Based on catalyst concentration alteration (Figure 1) as well as the temperature and reaction time variation (Figure 2), it was revealed that the best conversion was achieved at the catalyst concentration of 3%, molar ratio of RNSO to methanol of 1:30, reaction temperature of 60℃, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal in kapok randu seed oil using methanol reactant and sulfuric acid catalyst was 60℃ and reaction time of 120 minutes (Kusumaningtyas et al., 2019). Among the promising way to enhance the reaction conversion is by increasing the reaction temperature to 65℃ and applying higher molar ratio of the reactants as accomplished by Chai et al. (2014). In this work, the lowest FFA content obtained among all the experiments conducted was 4.01%. It didn't match with the standard limitation of FFA content for base catalyzed transesterification (2%). Therefore, response surface methodology optimization was then carried out to predict the optimum operation condition of the esterification reaction which can yield the 2% FFA content of RNSO.

Response Surface Methodology (RSM) Analysis

The result of the FFA removal was under the targeted value of FFA content (maximum 2%). Thus, optimization using response surface methodology (RSM) will be beneficial for designing the operation condition to achieve the targeted conversion. RSM is a set of mathematical and statistical tools which can be used for developing empirical model which correlate the reaction conversion or the yield of product with the significant process parameters (Veljković et al., 2019). Application of this tool has been found to be valuable to reduce the experimental cost (Liu et al., 2018). However, there are several models provided for the optimization using RSM. Hence, the suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. The similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this study, the best polynomial model will be useful to be applied in the future work for designing the experiment condition and improving the conversion of the reaction. To select the

model, combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification in RNSO using sulfuric acid catalyst were investigated. These variables were used for the optimization using RSM since they were the main parameters studied in experimental work. Experiments with the different combination of the three variables were conducted and calculated statistically using experimental design which was based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial (Rodríguez-Ramírez et al., 2020). This full factorial design is the most commonly applied in RSM optimization (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Table 3

Experimental Design Using Box-Behnken Methodology (BBD) which Equipped with the Experimental Data and Predictive Result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25
2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The four polynomial models, namely linear, interactive (2FI), quadratic, and cubic were used to predict the response variable to the experimental data. Two types of tests, i.e., sequential model sum of squares and model summary were used as the basic for the polynomial model determination which is suitable for optimizing the FFA conversion. The result is shown in Tables 4 and 5, respectively.

Table 4

Sequential Model Sum of Squares Test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Qubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						
Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Qubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Table 5

Model Summary Test

Component	Std. Dev	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content					
Linear	**0.0250**	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	0.2604	-0.8490	-	0.9989
Quadratik	**0.0221**	**0.9172**	**-**	**Suggested**	**0.0221**
Qubic	**-**	-	-	Aliased	**-**
Model summary of FFA Conversion					
Linear	**0.0249**	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	**0.9171**	**-**	**Suggested**	**0.0222**
Qubic	**-**	-	-	Aliased	**-**

Based on the result shown in Tables 4 and 5, it was acquired that the quadratic model was justified as the most suitable model for optimizing the FFA content and conversion in the esterification using sulfuric acid catalyst. The basis of the selection of the quadratic model was the lowest p-value, the highest value of adjusted R^2, and the highest value of predicted R^2. Table 4 reveals that the quadratic model provided the lowest p-value. Table 5 shows that the highest value of adjusted R^2 was provided by the quadratic model. Meanwhile, the predicted R^2 for the quadratic model didn't appear in Table 5 since the value was precisely closed to 1. In contrast, the values of actual R^2 were not presented in Table 5 since this table depicted the summary of the model test. The actual R^2 values were advanced investigated based on the values of predicted R^2. Based on the values of the p-value, adjusted R^2, and predicted R^2 attained, the quadratic model was found as the most suitable model and further analyzed using ANOVA. This finding is in line the result analysis of Maran & Priya (2015), which suggested that quadratic model was the most appropriate model.

The empirical model which was expressed using quadratic model with the interaction obtained from the experimental data based on the RSM was modified into polynomial equation. The final equation for FFA content and FFA conversion optimization are presented in the Equations 1 dan 2, respectively.

FFA Content (%) = 16.5 – 0.306 A – 2.2 B + 0.014 C – 0.0059 AB – 0.000042 AC + 0.0005 BC + 0.0026 A^2 + 0.54 B^2 – 0.00014 C^2 (1)

FFA Conversion (%) = 10.63 + 1.66 A + 11.91B – 0.081 C + 0.032 AB + 0.00026 AC + 0.0026 BC – 0.014 A^2 – 2.94 B^2 + 0.00075 C^2 (2)

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6

ANOVA Regression Model to Predict the FFA Conversion Using Sulfuric Acid Catalyst

Source	*Sum of square*	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	

X_{23}	0.0992	1	0.0992	0.0120	0.9197
X_1^2	4.37	1	4.37	0.5278	0.5201
X_2^2	315.17	1	315.17	38.08	0.0086
X_3^2	1.04	1	1.04	0.1258	0.7463
Residual	24.83	3	8.28		
Cor Total	1197.58	12			
Adeq prec	12.46				

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential which could cause the model unsuccessful to predict the value of response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision is the measure of the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. Ratio of 12.46 resulted in this work denoted that the inputted signal was appropriate.

Validation of the model capability in predicting is necessary to ensure the accuracy of model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the calculation using the model was close to the experimental data. It was indicated by the point of the response values of prediction and experimental just about the 45^o line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

The model suitability was further diagnosed by constructing a plot between the externally studied residuals with the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error which could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the result of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimization in the FFA esterification using sulfuric acid catalyst. The graphical illustration, termed response surface, is

frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).

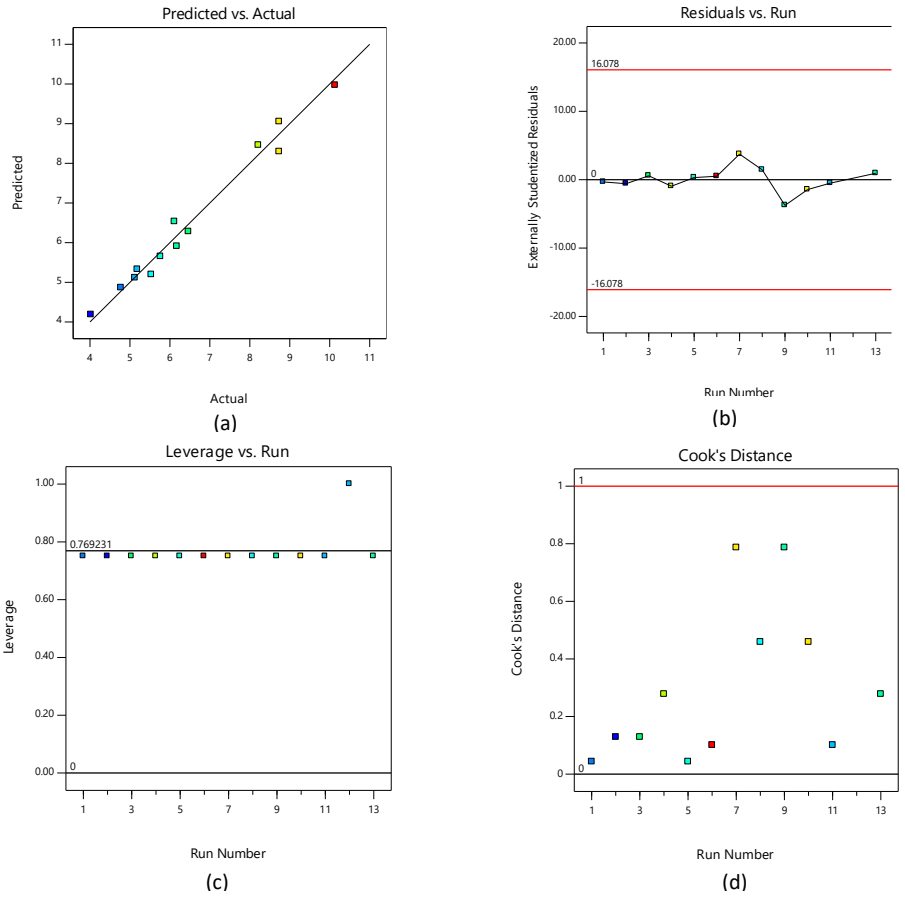

Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

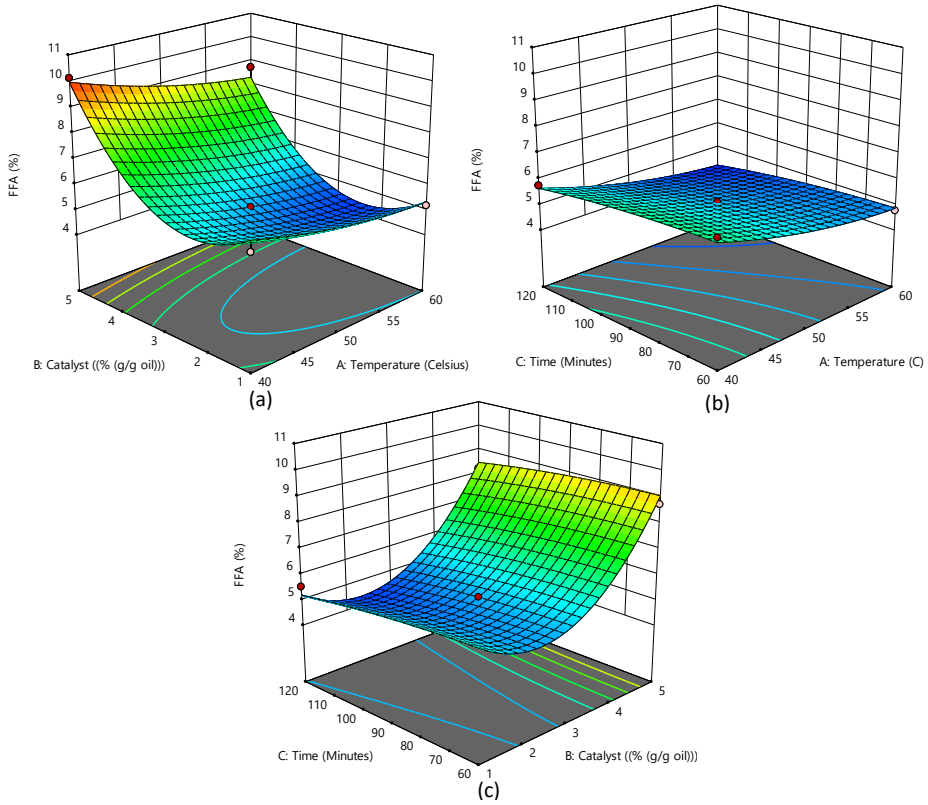

Figure 4. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Content. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50°C.

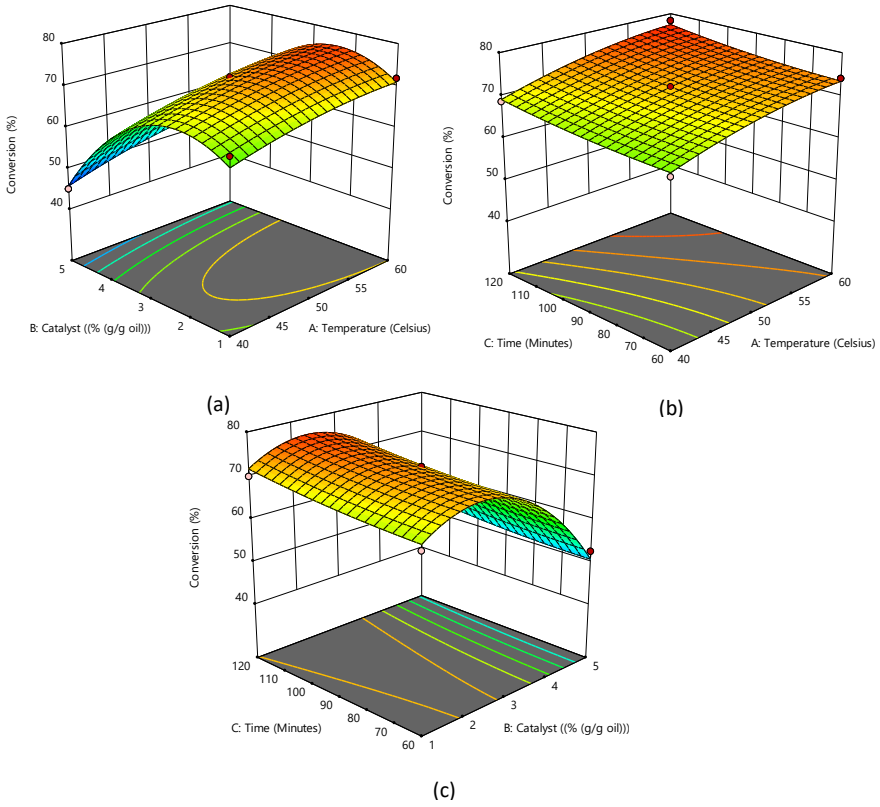

Figure 5. Three Dimensional (3D) Response Surface of the Effect of the Process Condition to the FFA Conversion. (a) Reaction Time = 90 min; (b) Catalyst Concentration = 5 (g/g RNSO); and (c) Reaction Temperature = 50℃.

The significant variables affecting the FFA content and the FFA conversion were temperature and catalyst concentration as demonstrated in Figures 4 and 5, respectively. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to 60℃. Additionally, the increasing of catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, additional amount of catalyst employment did not result in the higher reaction conversion as well as the FFA

removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

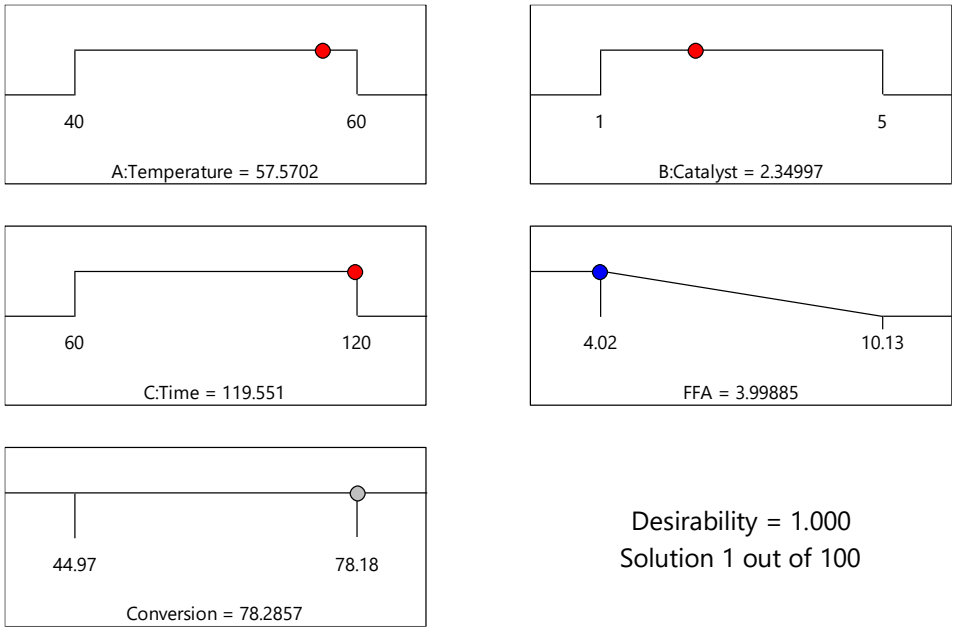

Figure 6. Optimization of FFA Conversion Using RSM (Quadratic Model)

In this work, Derringer Method was employed for the FFA conversion and FFA removal optimization in the esterification using sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as multi response problem based on Multi-criteria Decision Making. In this case, desirability approach is often employed as a vigorous instrument for optimization in multi response system. Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided undesired response. On the other hand, the value 1 indicates to the optimal condition of the parameter evaluated (Amdoun et al., 2018).

Based on the RSM simulation, it was revealed that the optimum conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 ^{o}C, catalyst concentration 1.98% g/g RNSO, and reaction time of 119.95 minutes. At this operation condition, the value of the desirability ramp was 1 (Figure 6). The result fitted the experimental data and indicated the accuracy of the model. The similar method of optimization applying desirability function was also described by (Mourabet et al., 2017).

To predict the operation condition to achieve the FFA content of maximum 2%, extrapolation using RSM was carried out. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration, and reaction time were 58.97℃, 3%, and 194.9 minutes, respectively, whereas, molar ratio of oil to methanol was fixed at 1:30. The FFA conversion achieved was estimated 89.3%.

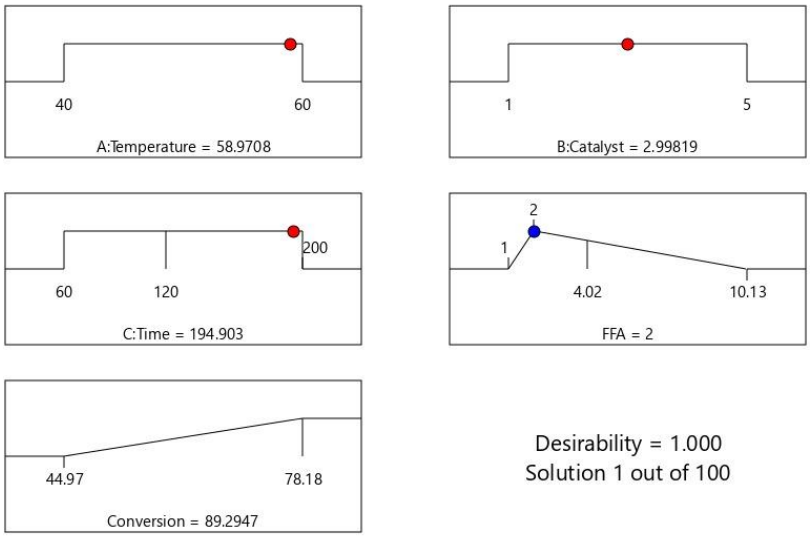

Figure 7. RSM Prediction of Operation Condition on the FFA Esterification Using Sulfuric Acid Catalyst to Decrease the FFA Content to 2%

The result has shown that RSM is simple and effective for process optimization. Furthermore, the combination of RSM and desirability function leads to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al., (2018). This study is significant to provide the optimum operation condition for reducing the FFA in CNSO in order to fulfill the allowable level of FFA content before it is used as feedstock for biodiesel production via base catalyzed transesterification reaction.

CONCLUSION

The experimental work of FFA esterification in RNSO with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition at the reaction temperature of 60℃, reaction time of 120 minutes, molar ratio of RNSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. This value was not match with the maximum acceptable value of FFA content for alkaline catalyzed transesterification (2%). The RSM was performed to estimate the optimal operation condition for achieving the FFA content of 2%. The RSM model analysis demonstrated that the quadratic model was the most suitable model for optimization of this process in the future work. The RSM extrapolation predicted that the FFA content of 2% can be obtained at the reaction temperature, catalyst concentration, and reaction time of 58.97℃, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30.

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06-Sep-2021

Dear Author(s),

I am writing to you in reference to an article entitled, “Optimization of Free Fatty Acid Removal in Nyamplung Seed Oil (Callophyllum inophylum L.) using Response Surface Methodology Analysis” author(s): Kusumaningtyas, Ratna; Prasetiawan, Haniif; Putri, Radenrara; Triwibowo, Bayu; Kurnita, Siti ; Anggraeni, Nanda ; Veny, Harumi; HAMZAH, FAZLENA; MUHD RODHI, MIRADATUL NAJWA submitted to Pertanika on 31-Mar-2021 for intended publication in JST.

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Thank you

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Optimisation of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum* L.) using Response Surface Methodology Analysis

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Optimisation of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophylum L.*) using Response Surface Methodology Analysis

Ratna Dewi Kusumaningtyas[1]*, Haniif Prasetiawan[1], Radenrara Dewi Artanti Putri[1], Bayu Triwibowo[1], Siti Choirunisa Furi Kurnita[1], Nanda Dwi Anggraeni[1], Harumi Veny[2], Fazlena Hamzah[2] and Miradatul Najwa Muhd Rodhi[2]

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ABSTRACT

Nyamplung seed (*Calophyllum inophyllum L.*) oil is a prospective non-edible vegetable oil as biodiesel feedstock. However, it cannot be directly used in the alkaline catalysed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalysed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18%, and the FFA concentration was decreased to 4.01% at the temperature of 60°C and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable FFA conversion optimisation. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09°C,

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1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% could be obtained at the temperature, catalyst concentration, and reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30. The results disclosed that RSM is an appropriate statistical method for optimising the process variable in the esterification reaction to obtain the targeted value of FFA.

Keywords: Biodiesel, Box-Behnken, esterification, FFA, quadratic model, RSM, sulfuric acid

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. To date, fossil energy still dominates the energy supply worldwide (Ghasemian et al., 2020). However, crude oil production in some countries shows a declining trend, which is not in balance with the energy need. Besides, the utilisation of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, contributing to global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilisation have led to the increasing interest in renewable energy research. In recent days, many countries implement the policy to use fossil fuel and biofuel blending to ensure energy sustainability and security. Biodiesel is a viable biofuel that can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is non-toxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristics, a high flash point that ensures safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Application of biodiesel/diesel fuel blends in diesel engines shows a good combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is a fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of the current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, at least three moles of alcohol are required to achieve complete conversion of one mol of triglycerides to alkyl esters (Islam et al., 2014). The most common catalyst for biodiesel production is an alkaline catalyst such as KOH, NaOH, or solid base catalyst. The transesterification process using an alkaline catalyst is cheap and easy.

Some potential biodiesel feedstocks in Indonesia are crude palm oil, jatropha oil, and coconut oil. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among Indonesia's the prospective local non-edible oil for biodiesel production

is nyamplung (*Calophyllum inophyllum L.*) seed oil (Musta et al., 2017; Silitonga et al., 2014). *Calophyllum inophyllum L* is extensively planted in Indonesia, and the nyamplung seed oil can be purchased from the local farmers (Ong et al., 2019). In addition, Atabani and César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed good properties and good engine performance and emission in diesel machines.

However, crude nyamplung seed oil (CNSO) usually contains gum and high free fatty acid (FFA). A high amount of FFA in the feedstock is not desirable in alkaline catalysed transesterification since it can react with the base catalyst, yielding the soap and diminishing the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Generally, the maximum tolerable amount of FFA in base-catalysed transesterification is 2%. Thus, a pre-treatment step is necessary to reduce the FFA content in nyamplung seed oil to a maximum level of 2% prior to transesterification reaction. FFA removal in CNSO can be conducted through an esterification reaction using methanol in the presence of an acid catalyst. There are several types of acid catalysts for FFA esterification. They are categorised into the homogenous acid catalysts, for instance, sulfuric acid, para-toluene sulfonic acid, phosphoric acid, and hydro, and HCl (Harun et al., 2018; Murad et al., 2018) and the heterogenous ones, such as Amberlyst 15, sulfated zirconia, niobic acid, zeolite, and tin (II) chloride (Banchero & Gozzelino, 2018; Dal Pozzo et al., 2019; Kusumaningtyas et al., 2014) Homogenous catalyst, particularly sulfuric acid, has been found as an efficient and economic catalyst for FFA esterification both at laboratory and industrial scales (Banani et al., 2015; Chai et al., 2014; Gebremariam & Marchetti, 2018).

Therefore, sulfuric acid was selected as the catalyst for the FFA removal via the esterification reaction of CNSO oil in this work. The investigation included experimental work and the analysis using response surface methodology (RSM) to determine the optimal operation condition, which yielded the targeted FFA final value of 2%. The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction. The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimisation. The study on the FFA esterification in CNSO in the presence of a sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimisation, has never been reported in the literature.

MATERIALS AND METHODS

Materials

The material used in this work were: crude nyamplung seed oil (CNSO), phosphoric acid (p.a., Merck), methanol (industrial grade, form local supplier), ethanol (analytical grade,

from Merck), KOH (analytical grade, from Merck), oxalic acid (analytical grade, from Merck), sulfuric acid (analytical grade, from Merck), distilled water (analytical grade, from a local supplier), and phenolphthalein indicator (analytical grade, from Merck).

Nyampung Seed Oil Characterisation

Prior to the esterification reaction, the crude nyamplung seed oil (CNSO) was first degummed using phosphoric acid to remove its gum content, resulting in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were then characterised to reveal their properties. First, the fatty acid composition was determined using Gas Chromatography-Mass Spectroscopy (GC-MS Perkin Elmer, GC Clarus 680, MS Clarus SQ 8T), similar to our previous work (Kusumaningtyas et al., 2016). Next, density measurement was conducted using a pycnometer (Taghizade, 2016). Then, viscosity determination was carried out using viscometer bath Stanhope-Seta KV6 tube 350 CFO. Finally, acid value tests were accomplished based on the AOCS acid-base titration method (Banchero & Gozzelino, 2018).

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using a hot plate at 70°C. Next, sulfuric acid with a concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using a magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm distilled water (40-50°C in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated. Then, the two layers were formed. The top and bottom layers were refined nyamplung seed oil (RNSO) and gum, respectively. To remove the water content, the RNSO was then heated using the oven at 105°C until it reached the constant weight.

FFA Removal

The FFA removal was conducted via an esterification reaction with methanol employing sulfuric acid. First, RNSO and methanol were weighed to obtain the molar ratio of RNSO and methanol of 1:30. Then, RNSO was introduced into the three necks flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at an exact temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into the reactor. The reaction temperatures were varied at 40°C, 50°C, and 60°C. Afterwards, the sulfuric acid catalyst was added at a specific concentration (1%, 3%, 5%, 7% w/w RNSO). The reaction was carried out for 120 minutes. A constant mixing using a magnetic stirrer with a speed of 1000 rpm was performed to certify the homogeneous reaction. The total experimental running was 7

experiments with different operating conditions. The sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples was calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

Response Surface Methodology

Response Surface Methodology using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the Box-Behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic, were evaluated to determine the most appropriate model for optimisation. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of crude nyamplung seed oil (CNSO) and refined nyamplung seed oil (RNSO), which has undergone a degumming process, were demonstrated in Table 1. The degumming process aims for reducing the gum content. Besides, degumming has also brought about a better characteristic of the oil feedstock. It can be observed in Table 1, the density viscosity, acid number, and acidity of the RNSO were lower than CNSO. The decreasing value of density happened due to the losses of some heavy compounds such as gum. The degumming process also caused a lighter colour of the oil. It was due to removing the compounds which significantly affected the oil colour (Lamas et al., 2016). Thus, the degumming process has shown a better characteristic of the oil feedstock, leading to an effective transesterification reaction and a higher quality of biodiesel product.

Table 1
Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

The fatty acid composition in CNSO was determined using GC-MS, and the result was exhibited in Table 2. Based on this composition, the molecular weight of CNSO can be calculated. It was found that CNSO molecular weight was 869.74 g/mol and the most

dominant fatty acid in CNSO were oleic acid and linoleic acids. It is in good agreement with the fatty acid composition found by Aparamarta et al. (2020). The fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process did not significantly change the fatty acid composition.

Table 2
Crude Nyamplung Seed Oil (CNSO) fatty acid composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55
Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of Free Fatty Acid (FFA): Effect of Catalyst Concentration

Free fatty acid (FFA) removal was conducted via esterification reaction of RNSO and methanol in the presence of a sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied at 1%, 3%, 5%, and 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40°C, 50°C, and 60°C. Encinar et al. (2021) suggested the sulfuric acid catalyst concentration of 0.5% to 2% for the feedstock with an FFA content of 10.7%. The higher sulfuric catalyst concentration can be employed for the higher acidic vegetable oils. The molar ratio of oil to methanol referred to Chai et al. (2014), recommended the molar ratio of oil to methanol in the range of 1:20 to 1:60. Specifically, Marchetti & Errazu (2008) proposed the molar ratio of 1:30 as the optimal condition. On the other hand, the reaction temperature ratio was adjusted to the boiling point of the methanol. The reaction was run for 120 minutes, as suggested by Chai et al. (2014). The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

In Figure 1, reaction conversion increased at the catalyst concentration from 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in a higher possibility of reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the other hand, the apparent reaction conversion declined on the higher reaction concentration (5% to 7%) since the excessive amount of catalyst could provoke the side reaction and reduce the FFA conversion (Widiarti et al., 2017). The excessive employment of catalysts will correspondingly bring about the difficulty and higher costs in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the temperature of 60°C with a reaction

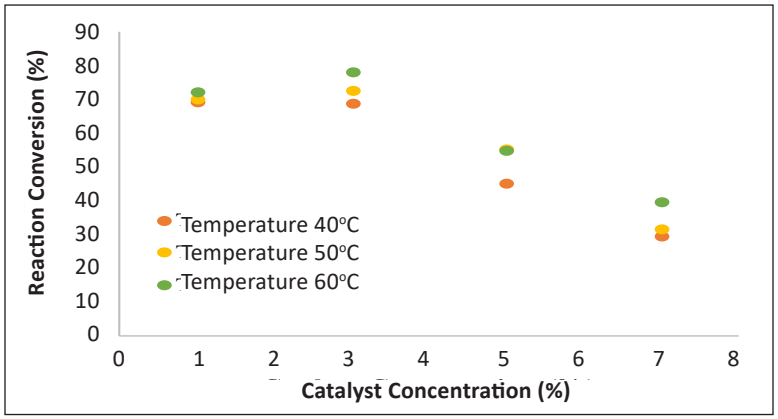


Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of RNSO to Methanol of 1:30

time of 120 minutes. The FFA content of such operation conditions was 4.01%. This value has not satisfied the maximum allowable FFA content of 2% for the transesterification reaction yet. Therefore, further, observation was conducted at different temperatures and reaction times.

Esterification of Free Fatty Acid (FFA): Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that the higher the reaction temperature, the higher removal of FFA occurred. This phenomenon was because the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increase in the reaction temperature raised the FFA conversion. This fact also agreed with the Arrhenius law, which states that the reaction rate is equivalent to the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. According to Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature rises.

As shown in Figure 2, it was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 to 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. Based on catalyst concentration alteration (Figure 1) as well as the temperature and reaction time variation (Figure 2), it was revealed that the best conversion was achieved at the catalyst concentration of 3%, molar ratio of RNSO to methanol of 1:30, reaction temperature of 60°C, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal in kapok randu seed oil using methanol reactant and the sulfuric acid catalyst was 60°C, and reaction time of 120 minutes (Kusumaningtyas et al.,

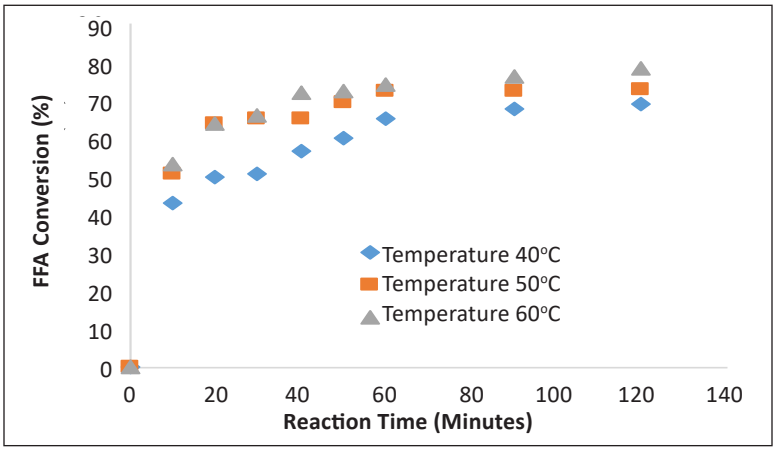


Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of RNSO and Methanol of 1:30

2019). The promising way to enhance the reaction conversion is by increasing the reaction temperature to 65°C and applying a higher molar ratio of the reactants, as accomplished by Chai et al. (2014). In this work, the lowest FFA content obtained among all the experiments conducted was 4.01%. It did not match FFA content's standard limitation for base catalysed transesterification (2%). Therefore, response surface methodology optimisation was then carried out to predict the optimum operating condition of the esterification reaction, yielding the 2% FFA content of RNSO.

Response Surface Methodology (RSM) Analysis

The result of the FFA removal was under the targeted value of FFA content (maximum 2%). Thus, optimisation using response surface methodology (RSM) will be beneficial for designing the operating condition to achieve the targeted conversion. RSM is a set of mathematical and statistical tools that can be used to develop an empirical model that correlates the reaction conversion or product yield with the significant process parameters (Veljković et al., 2019). The application of this tool is valuable to reduce the experimental cost (Liu et al., 2018). However, there are several models provided for optimisation using RSM. Hence, a suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. Similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this study, the best polynomial model will be useful for future work to design the experiment condition and improve the conversion of the reaction. A combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification in RNSO using sulfuric acid catalyst were investigated to

select the model. These variables were used to optimise using RSM since they were the main parameters studied in experimental work. Experiments with the different combinations of the three variables were conducted and calculated statistically using an experimental design based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial (Rodríguez-Ramírez et al., 2020). This complete factorial design is the most commonly applied in RSM optimisation (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Table 3
Experimental Design Using Box-Behnken Methodology (BBD), which equipped with the experimental data and predictive result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25
2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The four polynomial models, namely linear, interactive (2FI), quadratic, and cubic, were used to predict the response variable to the experimental data. In addition, two types of tests, i.e., a sequential model sum of squares and model summary, were used as the basis for the polynomial model determination, which is suitable for optimising the FFA conversion. The result is shown in Tables 4 and 5, respectively.

Based on the result shown in Tables 4 and 5, it was acquired that the quadratic model was justified as the most suitable model for optimising the FFA content and conversion in the esterification using a sulfuric acid catalyst. The basis of the selection of the quadratic model was the lowest p-value, the highest value of adjusted R^2, and the highest value of predicted R^2. Table 4 reveals that the quadratic model provided the lowest p-value. Table 5 shows that the quadratic model provided the highest value of adjusted R^2. Meanwhile, the predicted R^2 for the quadratic model did not appear in Table 5 since the value was precisely closed to 1. In contrast, the actual R^2 were not presented in Table 5 since this table depicted

Table 4
Sequential model sum of squares test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Cubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						
Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Cubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Table 5
Model summary test

Component	Std. Dev	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content					
Linear	**0.0250**	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	0.2604	-0.8490	-	0.9989
Quadratic	**0.0221**	**0.9172**	**-**	**Suggested**	**0.0221**
Cubic	**-**	-	-	Aliased	**-**
Model summary of FFA Conversion					
Linear	**0.0249**	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	**0.9171**	**-**	**Suggested**	**0.0222**
Cubic	**-**	-	-	Aliased	**-**

the summary of the model test. Therefore, the actual R^2 values were advanced investigated based on the values of predicted R^2. Based on the values of the p-value, adjusted R^2, and predicted R^2 attained, the quadratic model was found the most suitable model and further analysed using ANOVA. This finding is in line with the result analysis of Maran & Priya (2015), which suggested that the quadratic model was the most appropriate.

The empirical model, expressed using the quadratic model with the interaction obtained from the experimental data based on the RSM, was modified into a polynomial equation.

The final equation for FFA content and FFA conversion optimisation is presented in Equations 1 and 2, respectively.

$$\text{FFA Content (\%)} = 16.5 - 0.306\,A - 2.2\,B + 0.014\,C - 0.0059\,AB - 0.000042\,AC + 0.0005\,BC + 0.0026\,A^2 + 0.54\,B^2 - 0.00014\,C^2 \quad (1)$$

$$\text{FFA Conversion (\%)} = 10.63 + 1.66\,A + 11.91B - 0.081\,C + 0.032\,AB + 0.00026\,AC + 0.0026\,BC - 0.014\,A^2 - 2.94\,B^2 + 0.00075\,C^2 \quad (2)$$

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6
ANOVA regression model to predict the FFA conversion using sulfuric acid catalyst

Source	Sum of square	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	
X_{23}	0.0992	1	0.0992	0.0120	0.9197	
X_1^2	4.37	1	4.37	0.5278	0.5201	
X_2^2	315.17	1	315.17	38.08	0.0086	
X_3^2	1.04	1	1.04	0.1258	0.7463	
Residual	24.83	3	8.28			
Cor Total	1197.58	12				
Adeq prec	12.46					

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential, which could cause the model unsuccessful in predicting the value of the response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision measures the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. A ratio of 12.46 resulted in this work, denoted that the inputted signal was appropriate.

Validation of the model capability in predicting is necessary to ensure the accuracy of the model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the model's calculation was close to the experimental data. It was indicated by the

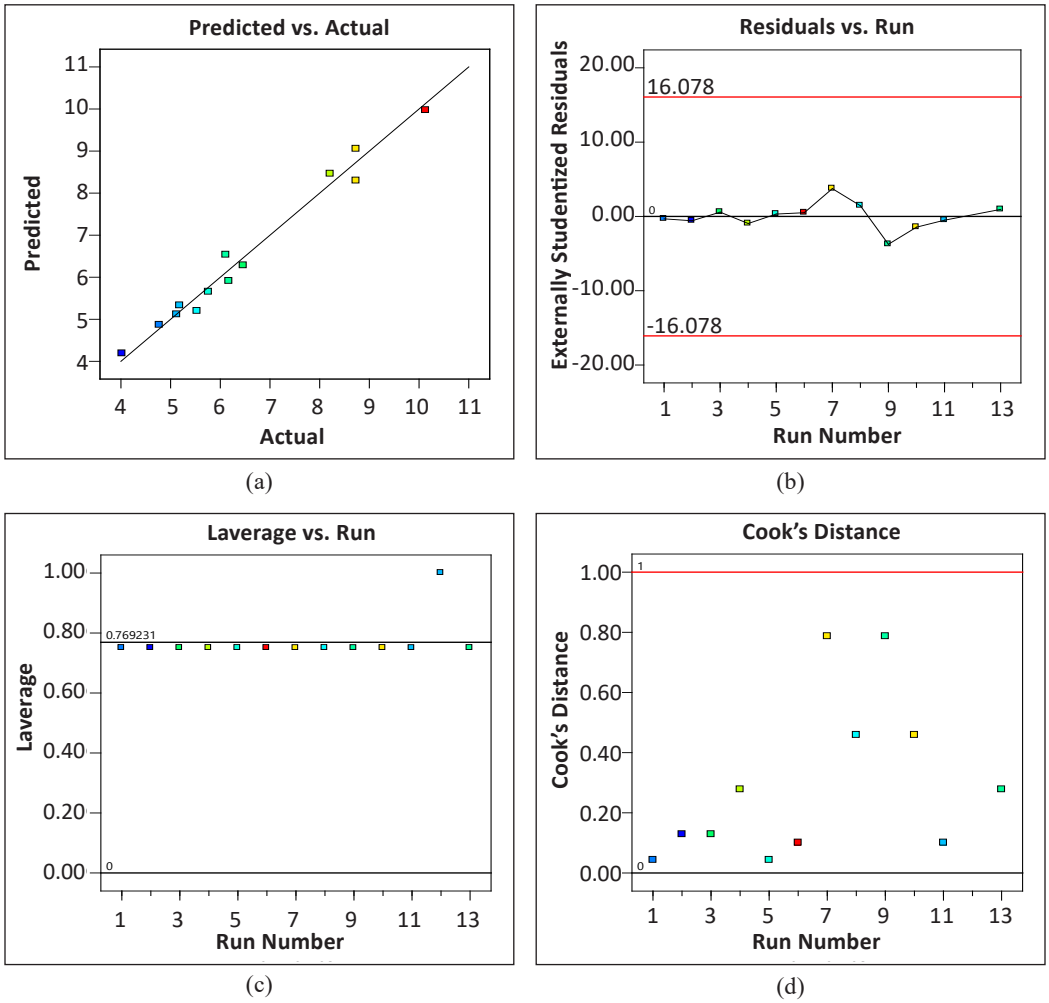
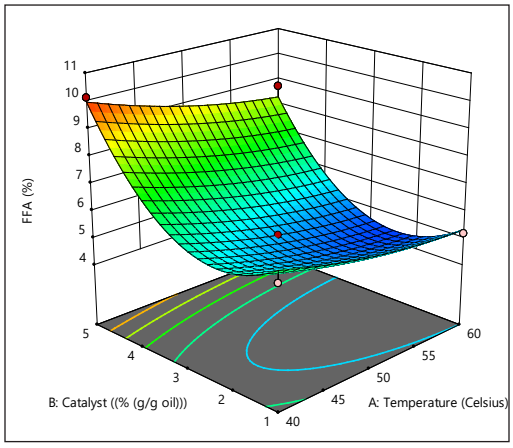


Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

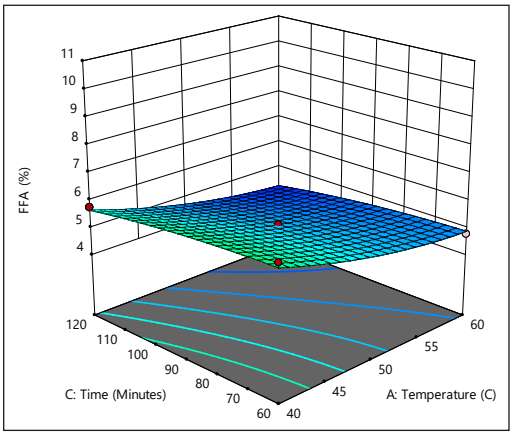
point of the prediction and experimental response values just about the 45° line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

The model suitability was further determined by constructing a plot between the externally studied residuals and the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error that could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the results of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimisation in the FFA esterification using a sulfuric acid catalyst. The graphical illustration, termed response surface, is frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).

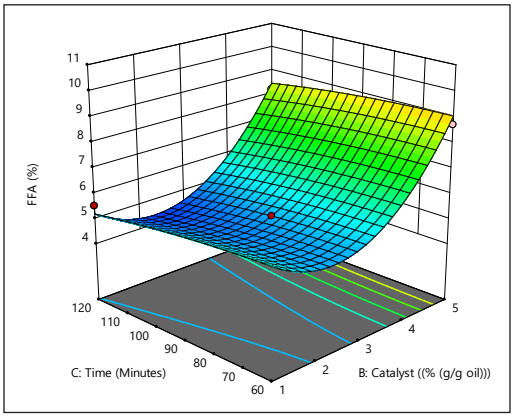
The significant variables affecting the FFA content and conversion were temperature and catalyst concentration as demonstrated in Figures 4 and 5. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to



(a)



(b)



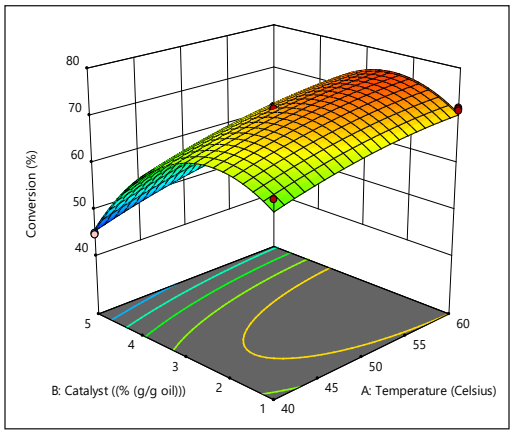
(c)

Figure 4. Three dimensional (3D) response surface of the effect of the process condition to the FFA content. (a) Reaction time = 90 min; (b) Catalyst concentration = 5 (g/g RNSO); and (c) Reaction temperature = 50°C.

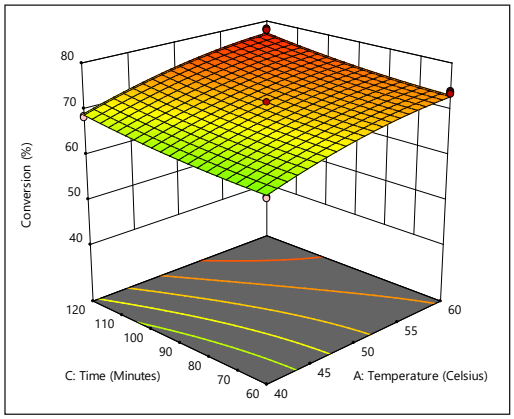
60°C. Additionally, increasing catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, an additional amount of catalyst employment did not result in the higher reaction conversion and the FFA removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

In this work, the Derringer method was employed for the FFA conversion and FFA removal optimisation in the esterification using a sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as a multi-response problem based on Multi-criteria Decision Making. In this case, the desirability approach is often employed as a vigorous instrument for optimisation in a multi-response system. The Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided an undesired response. On the other hand, the value 1 indicates the optimal condition of the parameter evaluated (Amdoun et al., 2018).

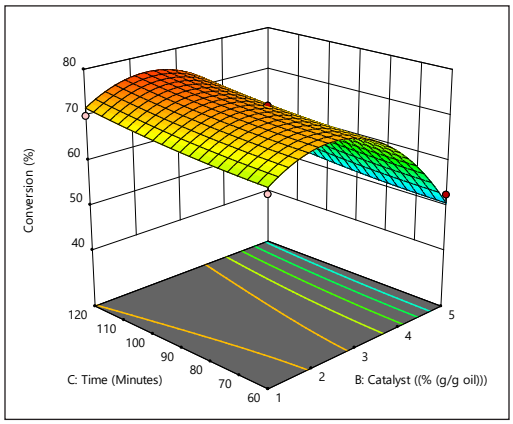
Based on the RSM simulation, it was revealed that the optimum conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 °C, catalyst concentration 1.98% g/g RNSO, and reaction time of 119.95 minutes. At this operation condition, the value of the desirability ramp



(a)



(b)



(c)

Figure 5. Three dimensional (3D) Response surface of the effect of the process condition to the FFA conversion. (a) Reaction time = 90 min; (b) Catalyst concentration = 5 (g/g RNSO); and (c) Reaction temperature = 50°C.

was 1 (Figure 6). The result fitted the experimental data and indicated the accuracy of the model. A similar method of optimisation applying desirability function was also described by (Mourabet et al., 2017).

Extrapolation was performed using RSM to predict the operating conditions and achieve a maximum of 2% FFA content. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration,

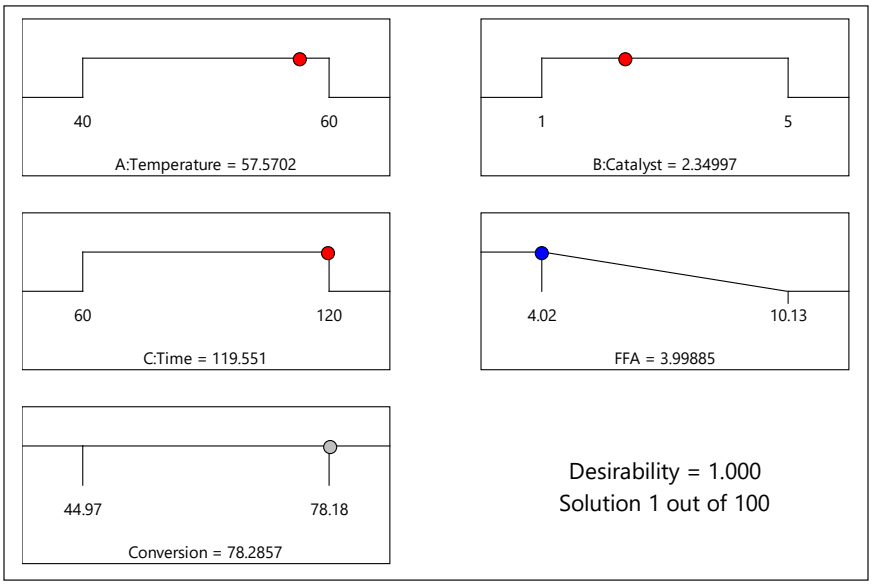


Figure 6. Optimisation of FFA conversion using RSM (Quadratic model)

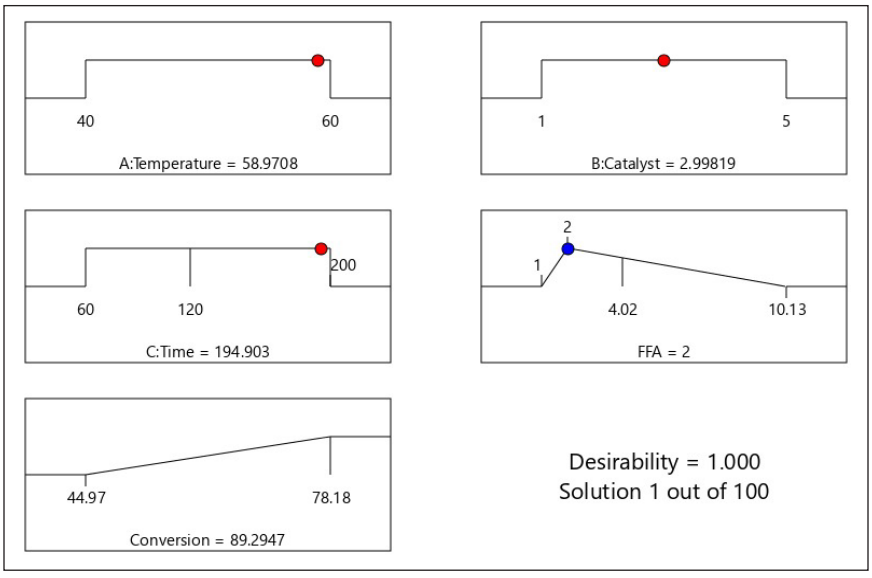


Figure 7. RSM prediction of operation condition on the FFA esterification using sulfuric acid catalyst to decrease the FFA content to 2%

and reaction time were 58.97°C, 3%, and 194.9 minutes, respectively, whereas the molar ratio of oil to methanol was fixed at 1:30. Therefore, the FFA conversion achieved was estimated at 89.3%.

The result has shown that RSM is simple and effective for process optimisation. Furthermore, the RSM and desirability function combination lead to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al. (2018). This study is significant in providing the optimum operating condition for reducing the FFA in CNSO to fulfil the allowable level of FFA content before being used as feedstock for biodiesel production via base catalysed transesterification reaction.

CONCLUSION

The experimental work of FFA esterification in RNSO with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition at the reaction temperature of 60°C, a reaction time of 120 minutes, the molar ratio of RNSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. This value did not match the maximum acceptable FFA content value for alkaline catalysed transesterification (2%). The RSM was performed to estimate the optimal operation condition for achieving the FFA content of 2%. The RSM model analysis demonstrated that the quadratic model was the most suitable for optimising this process in future work. The RSM extrapolation predicted that the FFA content of 2% could be obtained at the reaction temperature, catalyst concentration, reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30.

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Optimisation of Free Fatty Acid Removal in Nyamplung Seed Oil (*Callophyllum inophyllum* L.) using Response Surface Methodology Analysis

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ABSTRACT

Nyamplung seed (*Calophyllum inophyllum* L.) oil is a prospective non-edible vegetable oil as biodiesel feedstock. However, it cannot be directly used in the alkaline catalysed transesterification reaction since it contains high free fatty acid (FFA) of 19.17%. The FFA content above 2% will cause saponification reaction, reducing the biodiesel yield. In this work, FFA removal was performed using sulfuric acid catalysed esterification to meet the maximum FFA amount of 2%. Experimental work and response surface methodology (RSM) analysis were conducted. The reaction was conducted at the fixed molar ratio of nyamplung seed oil and methanol of 1:30 and the reaction times of 120 minutes. The catalyst concentration and the reaction temperature were varied. The highest reaction conversion was 78.18%, and the FFA concentration was decreased to 4.01% at the temperature of 60°C and reaction time of 120 minutes. The polynomial model analysis on RSM demonstrated that the quadratic model was the most suitable FFA conversion optimisation. The RSM analysis exhibited the optimum FFA conversion of 78.27% and the FFA content of 4%, attained at the reaction temperature, catalyst concentration, and reaction time of 59.09°C,

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1.98% g/g nyamplung seed oil, and 119.95 minutes, respectively. Extrapolation using RSM predicted that the targeted FFA content of 2% could be obtained at the temperature, catalyst concentration, and reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, with a fixed molar ratio of oil to methanol of 1:30. The results disclosed that RSM is an appropriate statistical method for optimising the process variable in the esterification reaction to obtain the targeted value of FFA.

Keywords: Biodiesel, Box-Behnken, esterification, FFA, quadratic model, RSM, sulfuric acid

INTRODUCTION

Population, economic, and industry growth have intensified the global energy demand. To date, fossil energy still dominates the energy supply worldwide (Ghasemian et al., 2020). However, crude oil production in some countries shows a declining trend, which is not in balance with the energy need. Besides, the utilisation of fossil fuel currently also faces an environmental challenge as its combustion becomes the major source of carbon dioxide emission. Carbon dioxide is among the most dominant greenhouse gasses, contributing to global warming and climate change (Paraschiv & Paraschiv, 2020). The issues on the fossil fuel supply depletion and the negative environmental effect of fossil fuel utilisation have led to the increasing interest in renewable energy research. In recent days, many countries implement the policy to use fossil fuel and biofuel blending to ensure energy sustainability and security. Biodiesel is a viable biofuel that can be used as pure or in blends with diesel fuel. This alternative fuel is prospective for large scale production and application since it is non-toxic, low sulfur and aromatics content, biodegradable, and simple to use. Moreover, it holds neutral carbon characteristics, a high flash point that ensures safety in handling and storage, good lubricity, and high oxygen (Corach et al., 2017; Dey et al., 2021). Application of biodiesel/diesel fuel blends in diesel engines shows a good combustion, performance and emission reduction, especially for B20 or 20% biodiesel in the biodiesel-diesel fuel mixture (Mubarak et al., 2021).

Biodiesel is a fatty acid methyl ester derived from vegetable oils and/or animal fats. Most of the current industrial production of biodiesel from vegetable oils is achieved through transesterification (Aboelazayem et al., 2018; Demirbas, 2006). Theoretically, in transesterification, at least three moles of alcohol are required to achieve complete conversion of one mol of triglycerides to alkyl esters (Islam et al., 2014). The most common catalyst for biodiesel production is an alkaline catalyst such as KOH, NaOH, or solid base catalyst. The transesterification process using an alkaline catalyst is cheap and easy.

Some potential biodiesel feedstocks in Indonesia are crude palm oil, jatropha oil, and coconut oil. However, currently, the non-edible vegetable oil is preferred as biodiesel raw material to avoid the conflict between food and energy need (Kusumaningtyas et al., 2014). Among Indonesia's the prospective local non-edible oil for biodiesel production

is nyamplung (*Calophyllum inophyllum* L.) seed oil (Musta et al., 2017; Silitonga et al., 2014). *Calophyllum inophyllum L* is extensively planted in Indonesia, and the nyamplung seed oil can be purchased from the local farmers (Ong et al., 2019). In addition, Atabani and César (2014) reported that *Calophyllum inophyllum* methyl ester blended with diesel fuel (B10 and B20) revealed good properties and good engine performance and emission in diesel machines.

However, crude nyamplung seed oil (CNSO) usually contains gum and high free fatty acid (FFA). A high amount of FFA in the feedstock is not desirable in alkaline catalysed transesterification since it can react with the base catalyst, yielding the soap and diminishing the biodiesel yield. The desired amount of FFA in alkaline-catalyst is less than 0.5% to less than 3% w/w of oil (Arora et al., 2015). Generally, the maximum tolerable amount of FFA in base-catalysed transesterification is 2%. Thus, a pre-treatment step is necessary to reduce the FFA content in nyamplung seed oil to a maximum level of 2% prior to transesterification reaction. FFA removal in CNSO can be conducted through an esterification reaction using methanol in the presence of an acid catalyst. There are several types of acid catalysts for FFA esterification. They are categorised into the homogenous acid catalysts, for instance, sulfuric acid, para-toluene sulfonic acid, phosphoric acid, and hydro, and HCl (Harun et al., 2018; Murad et al., 2018) and the heterogenous ones, such as Amberlyst 15, sulfated zirconia, niobic acid, zeolite, and tin (II) chloride (Banchero & Gozzelino, 2018; Dal Pozzo et al., 2019; Kusumaningtyas et al., 2014). Homogenous catalyst, particularly sulfuric acid, has been found as an efficient and economic catalyst for FFA esterification both at laboratory and industrial scales (Banani et al., 2015; Chai et al., 2014; Gebremariam & Marchetti, 2018).

Therefore, sulfuric acid was selected as the catalyst for the FFA removal via the esterification reaction of CNSO oil in this work. The investigation included experimental work and the analysis using response surface methodology (RSM) to determine the optimal operation condition, which yielded the targeted FFA final value of 2%. The final FFA level was aimed at 2% since it is the maximum acceptable FFA value for the subsequent transesterification reaction to avoid undesired saponification reaction. The work comprised the detailed analysis of several polynomial models on RSM to reveal the most appropriate model for optimisation. The study on the FFA esterification in CNSO in the presence of a sulfuric acid catalyst which involves the comprehensive analysis and selection of the various polynomial models in RSM for process optimisation, has never been reported in the literature.

MATERIALS AND METHODS

Materials

The material used in this work were: crude nyamplung seed oil, phosphoric acid (from Merck), methanol (industrial grade, form local supplier), ethanol (analytical grade, from

Merck), KOH (analytical grade, from Merck), oxalic acid (analytical grade, from Merck), sulfuric acid (analytical grade, from Merck), distilled water (analytical grade, from a local supplier), and phenolphthalein indicator (analytical grade, from Merck).

Nyampung Seed Oil Characterisation

Prior to the esterification reaction, the crude nyamplung seed oil was first degummed using phosphoric acid to remove its gum content, resulting in refined nyamplung seed oil (RNSO). Both CNSO and RNSO were then characterised to reveal their properties. First, the fatty acid composition was determined using Gas Chromatography-Mass Spectroscopy (GC-MS Perkin Elmer, GC Clarus 680, MS Clarus SQ 8T), similar to our previous work (Kusumaningtyas et al., 2016). Next, density measurement was conducted using a pycnometer (Taghizade, 2016). Then, viscosity determination was carried out using viscometer bath Stanhope-Seta KV6 tube 350 CFO. Finally, acid value tests were accomplished based on the AOCS acid-base titration method (Banchero & Gozzelino, 2018).

Degumming

Initially, 500 ml CNSO was introduced into 500 mL beaker glass and heated using a hot plate at 70°C. Next, sulfuric acid with a concentration of 0.3% w/w was added. The mixing was kept for 25 minutes using a magnetic stirrer to ensure the completion of the degumming reaction. After the reaction finished, the CNSO was inputted into the separating funnel and added with warm distilled water (40-50°C in temperature) for purification. The mixture of the degummed CNSO and water was settled for 24 hours until the gum was separated. Then, the two layers were formed. The top and bottom layers were refined nyamplung seed oil (RNSO) and gum, respectively. To remove the water content, the RNSO was then heated using the oven at 105°C until it reached the constant weight.

FFA Removal

The FFA removal was conducted via an esterification reaction with methanol employing sulfuric acid. First, RNSO and methanol were weighed to obtain the molar ratio of RNSO and methanol of 1:30. Then, RNSO was introduced into the three necks flask batch reactor and heated until it reached the reaction temperature. On the other flask, methanol was also heated at an exact temperature. When both RNSO and methanol attained the reaction temperature, methanol was then poured into the reactor. The reaction temperatures were varied at 40°C, 50°C, and 60°C. Afterwards, the sulfuric acid catalyst was added at a specific concentration (1%, 3%, 5%, 7% w/w RNSO). The reaction was carried out for 120 minutes. A constant mixing using a magnetic stirrer with a speed of 1000 rpm was performed to certify the homogeneous reaction. The total experimental running was 7

experiments with different operating conditions. The sample was taken periodically every 10 minutes for each experiment. Hence, the total sampling number was 31 times. The reaction conversions were calculated based on the FFA content of the sample using the procedure of our previous work. The FFA content of the samples was calculated using the standard KOH titration (Kusumaningtyas et al., 2018).

RSM

RSM using Design Expert 11 software was employed for statistical calculation using three different variables (reaction temperature, catalyst concentration, and reaction time) based on the Box-Behnken methodology (BBD). The four polynomials models in the RSM, namely linear, interactive (2FI), quadratic, and cubic, were evaluated to determine the most appropriate model for optimisation. The selected model was applied in this work.

RESULT AND DISCUSSION

CNSO and RNSO Characterization

The properties of CNSO and refined nyamplung seed oil (RNSO), which has undergone a degumming process, were demonstrated in Table 1. The degumming process aims for reducing the gum content. Besides, degumming has also brought about a better characteristic of the oil feedstock. It can be observed in Table 1, the density viscosity, acid number, and acidity of the RNSO were lower than CNSO. The decreasing value of density happened due to the losses of some heavy compounds such as gum. The degumming process also caused a lighter colour of the oil. It was due to removing the compounds which significantly affected the oil colour (Lamas et al., 2016). Thus, the degumming process has shown a better characteristic of the oil feedstock, leading to an effective transesterification reaction and a higher quality of biodiesel product.

Table 1
Properties of CNSO and RNSO

Properties	CNSO (Before Degumming)	RNSO (After Degumming)
Density (kg/m^3)	906	898
Viscosity (mm^2/s)	60.39	59.04
Acid Number (mg KOH/g)	0.38	0.36
Acidity (%)	19.18	18.39

The fatty acid composition in CNSO was determined using GC-MS, and the result was exhibited in Table 2. Based on this composition, the molecular weight of CNSO can be calculated. It was found that CNSO molecular weight was 869.74 g/mol and the most dominant fatty acid in CNSO were oleic acid and linoleic acids. It is in good agreement with

the fatty acid composition found by Aparamarta et al. (2020). The fatty acid composition was merely performed for the CNSO. Fatty acid analysis for the RNSO was discounted. Based on the slightly altering of the acid number of CNSO and RNSO exhibited in Table 1, it can be assumed that the degumming process did not significantly change the fatty acid composition.

Table 2
CNSO fatty acid composition

Fatty acid	Molecular Weight (g/mol)	Area (%)
Palmitic acid	256.2228	15.51
Linoleic acid	280.45	28.94
Oleic acid	282.52	40.55
Stearic acid	284.47	14,39
Arachidic acid	312.54	0.60

Esterification of FFA: Effect of Catalyst Concentration

FFA removal was conducted via esterification reaction of RNSO and methanol in the presence of a sulfuric acid catalyst. Sulfuric acid catalyst concentration was varied at 1%, 3%, 5%, and 7% w/w RNSO with the molar ratio of RNSO: methanol of 1: 30 and temperature of 40°C, 50°C, and 60°C. Encinar et al. (2021) suggested the sulfuric acid catalyst concentration of 0.5% to 2% for the feedstock with an FFA content of 10.7%. The higher sulfuric catalyst concentration can be employed for the higher acidic vegetable oils. The molar ratio of oil to methanol referred to Chai et al. (2014), recommended the molar ratio of oil to methanol in the range of 1:20 to 1:60. Specifically, Marchetti & Errazu (2008) proposed the molar ratio of 1:30 as the optimal condition. On the other hand, the reaction temperature ratio was adjusted to the boiling point of the methanol. The reaction was run for 120 minutes, as suggested by Chai et al. (2014). The effect of catalyst concentration on the FFA conversion is demonstrated in Figure 1.

In Figure 1, reaction conversion increased at the catalyst concentration from 1% to 3%. It was due to the decreasing of the activation energy by the addition of the catalyst. Thus, the collision between the particles was increased, resulting in a higher possibility of reaction occurrence. Accordingly, it enhanced the reaction rate and FFA conversion. On the other hand, the apparent reaction conversion declined on the higher reaction concentration (5% to 7%) since the excessive amount of catalyst could provoke the side reaction and reduce the FFA conversion (Widiarti et al., 2017). The excessive employment of catalysts will correspondingly bring about the difficulty and higher costs in the product separation. Based on the experiments, it was revealed that the optimum catalyst concentration was 3%, which resulted in the FFA conversion of 78.18% at the temperature of 60°C with a reaction time of 120 minutes. The FFA content of such operation conditions was 4.01%. This value

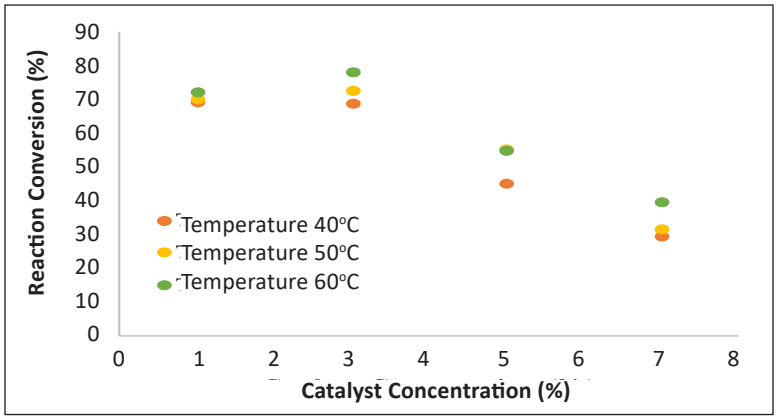


Figure 1. Effect of Catalyst Concentration on the FFA Conversion at the Reaction Time of 120 Minutes and Molar Ratio of RNSO to Methanol of 1:30

has not satisfied the maximum allowable FFA content of 2% for the transesterification reaction yet. Therefore, further, observation was conducted at different temperatures and reaction times.

Esterification of FFA: Effect of Temperature and Reaction Time

The influence of the reaction temperature and time was presented in Figure 2. It is shown that the higher the reaction temperature, the higher removal of FFA occurred. This phenomenon was because the higher reaction temperature will increase the molecular motion of each reactant species, improving the kinetics energy. Therefore, the increase in the reaction temperature raised the FFA conversion. This fact also agreed with the Arrhenius law, which states that the reaction rate is equivalent to the reaction temperature. Encinar et al. (2021) described that this phenomenon was common for the endothermic reaction. According to Le Chatelier's principle, the equilibrium shifts to the product formation as the temperature rises.

As shown in Figure 2, it was also found that the FFA conversion enhanced with the reaction time, but the enhancement was slower from 60 to 120 minutes. It means that the reaction was approaching the chemical equilibrium point at 120 minutes. Based on catalyst concentration alteration (Figure 1) as well as the temperature and reaction time variation (Figure 2), it was revealed that the best conversion was achieved at the catalyst concentration of 3%, molar ratio of RNSO to methanol of 1:30, reaction temperature of 60°C, and reaction time of 120 minutes with the FFA conversion of 78.18% and the FFA content of 4.01%. This result was in line with our previous work that reported that the optimum condition of FFA removal in kapok randu seed oil using methanol reactant and the sulfuric acid catalyst was 60°C, and reaction time of 120 minutes (Kusumaningtyas et al., 2019). The promising way to enhance the reaction conversion is by increasing the reaction

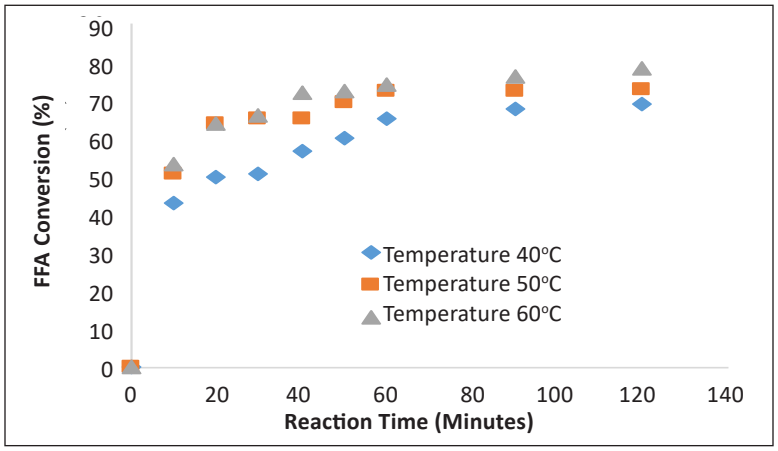


Figure 2. Effect of Temperature and Reaction Time on the FFA Conversion at the Catalyst Concentration of 3% w/w and Molar Ratio of RNSO and Methanol of 1:30

temperature to 65°C and applying a higher molar ratio of the reactants, as accomplished by Chai et al. (2014). In this work, the lowest FFA content obtained among all the experiments conducted was 4.01%. It did not match FFA content's standard limitation for base catalysed transesterification (2%). Therefore, response surface methodology optimisation was then carried out to predict the optimum operating condition of the esterification reaction, yielding the 2% FFA content of RNSO.

RSM Analysis

The result of the FFA removal was under the targeted value of FFA content (maximum 2%). Thus, RSM will be beneficial for designing the operating condition to achieve the targeted conversion. RSM is a set of mathematical and statistical tools that can be used to develop an empirical model that correlates the reaction conversion or product yield with the significant process parameters (Veljković et al., 2019). The application of this tool is valuable to reduce the experimental cost (Liu et al., 2018). However, there are several models provided for optimisation using RSM. Hence, a suitable model should be selected. In this work, four polynomial models (linear, interactive or 2FI, quadratic, and cubic) in RSM were evaluated to determine the most suitable model which fitted the experimental data. Similar models were also tested by Maran & Priya (2015) and Ahmad et al. (2020).

In this study, the best polynomial model will be useful for future work to design the experiment condition and improve the conversion of the reaction. A combination of the effects of the 3 independent variables (catalyst concentration, temperature, and reaction time) on the FFA esterification in RNSO using sulfuric acid catalyst were investigated to select the model. These variables were used to optimise using RSM since they were the main parameters studied in experimental work. Experiments with the different combinations

of the three variables were conducted and calculated statistically using an experimental design based on the Box-Behnken Methodology (BBD). The BBD is a self-reliant quadratic design which does not involve implanted factorial (Rodríguez-Ramírez et al., 2020). This complete factorial design is the most commonly applied in RSM optimisation (Veljković et al., 2019). The experimental design using BBD is shown in Table 3.

Table 3
Experimental Design Using Box-Behnken Methodology (BBD), which equipped with the experimental data and predictive result

Run	Temperature (A)	Catalyst Concentration (B)	Time (C)	FFA Conversion, %		% Error	FFA Content, %		% Error
				Exp	Prediction		Exp	Prediction	
1	60	3	60	74.07	74.10	0.05	4.77	4.97	4.25
2	60	3	120	78.18	78.75	0.73	4.02	4.24	5.46
3	40	3	60	64.9	66.67	2.73	6.46	6.30	2.52
4	50	5	120	55.41	56.88	2.65	8.21	8.44	2.76
5	40	3	120	68.7	71.00	3.35	5.76	5.61	2.53
6	40	5	90	44.97	47.97	6.67	10.13	9.94	1.88
7	60	5	90	52.56	56.84	8.14	8.73	8.35	4.30
8	50	1	120	69.96	72.15	3.13	5.53	5.22	5.66
9	40	1	90	66.8	64.84	2.94	6.11	6.54	7.10
10	50	5	60	52.56	52.08	0.91	8.73	9.09	4.07
11	60	1	90	71.85	71.14	0.98	5.18	5.43	4.83
12	50	3	90	72.17	73.36	1.64	5.12	5.15	0.53
13	50	1	60	66.48	67.98	2.25	6.17	5.99	3.00

The four polynomial models, namely linear, interactive (2FI), quadratic, and cubic, were used to predict the response variable to the experimental data. In addition, two types of tests, i.e., a sequential model sum of squares and model summary, were used as the basis for the polynomial model determination, which is suitable for optimising the FFA conversion. The result is shown in Tables 4 and 5, respectively.

Based on the result shown in Tables 4 and 5, it was acquired that the quadratic model was justified as the most suitable model for optimising the FFA content and conversion in the esterification using a sulfuric acid catalyst. The basis of the selection of the quadratic model was the lowest p-value, the highest value of adjusted R^2, and the highest value of predicted R^2. Table 4 reveals that the quadratic model provided the lowest p-value. Table 5 shows that the quadratic model provided the highest value of adjusted R^2. Meanwhile, the predicted R^2 for the quadratic model did not appear in Table 5 since the value was precisely closed to 1. In contrast, the actual R^2 were not presented in Table 5 since this table depicted the summary of the model test. Therefore, the actual R^2 values were advanced investigated based on the values of predicted R^2. Based on the values of the p-value, adjusted R^2, and

Table 4
Sequential model sum of squares test

Component	Sum of square	DF	Mean Square	F-value	p-value	Remarks
Sequential Sum of Square for FFA Content						
Mean	554.72	1	554.72			
Linear	**25.51**	**3**	**8.50**	**5.08**	**0.0250**	**Suggested**
2FI	0.0595	3	0.0198	0.0079	0.9989	
Quadratic	**14.16**	**3**	**4.72**	**16.85**	**0.0221**	**Suggested**
Cubic	0.8404	3	0.2801			Aliased
Residual	0.0000	0				
Total	595.30	13	45.79			
Sequential sum of square for FFA Conversion						
Mean	54097.44	1	54097.44			
Linear	**753.08**	**3**	**251.03**	**5.08**	**0.0249**	**Suggested**
2FI	1.74	3	0.5787	0.0078	0.9989	
Quadratic	**417.93**	**3**	**139.31**	**16.83**	**0.0222**	**Suggested**
Cubic	24.83	3	8.28			Aliased
Residual	0.0000	0				
Total	55295.02	13	4253.46			

Table 5
Model summary test

Component	Std. Dev	Adjusted R^2	Predicted R^2	Press	Remarks
Model Summary of FFA Content					
Linear	**0.0250**	**0.5050**	**0.2313**	**Suggested**	**0.0250**
2FI	0.9989	0.2604	-0.8490	-	0.9989
Quadratic	**0.0221**	**0.9172**	**-**	**Suggested**	**0.0221**
Cubic	**-**	-	-	Aliased	**-**
Model summary of FFA Conversion					
Linear	**0.0249**	**0.5051**	**0.2314**	**Suggested**	**0.0249**
2FI	0.9989	0.2606	-0.8492	-	0.9989
Quadratic	**0.0222**	**0.9171**	**-**	**Suggested**	**0.0222**
Cubic	**-**	-	-	Aliased	**-**

predicted R^2 attained, the quadratic model was found the most suitable model and further analysed using ANOVA. This finding is in line with the result analysis of Maran & Priya (2015), which suggested that the quadratic model was the most appropriate.

The empirical model, expressed using the quadratic model with the interaction obtained from the experimental data based on the RSM, was modified into a polynomial equation. The final equation for FFA content and FFA conversion optimisation is presented in Equations 1 and 2, respectively.

$$\text{FFA Content (\%)} = 16.5 - 0.306\,A - 2.2\,B + 0.014\,C - 0.0059\,AB - 0.000042\,AC + 0.0005\,BC + 0.0026\,A^2 + 0.54\,B^2 - 0.00014\,C^2 \quad (1)$$

$$\text{FFA Conversion (\%)} = 10.63 + 1.66\,A + 11.91B - 0.081\,C + 0.032\,AB + 0.00026\,AC + 0.0026\,BC - 0.014\,A^2 - 2.94\,B^2 + 0.00075\,C^2 \quad (2)$$

Statistical analysis for the quadratic model using ANOVA regression model is shown in Table 6.

Table 6
ANOVA regression model to predict the FFA conversion using sulfuric acid catalyst

Source	Sum of square	Degree of Freedom	Mean square	F value	p-value	Remarks
ANOVA for FFA Content						
Model	39.73	9	4.41	15.76	0.0221	significant
X_1	4.15	1	4.15	14.80	0.0310	
X_2	20.51	1	20.51	73.22	0.0034	
X_3	0.8515	1	0.8515	3.04	0.1796	
X_{12}	0.0552	1	0.0552	0.1971	0.6871	
X_{13}	0.0006	1	0.0006	0.0022	0.9653	
X_{23}	0.0036	1	0.0036	0.0129	0.9169	
X_1^2	0.1486	1	0.1486	0.5306	0.5191	
X_2^2	10.69	1	10.69	38.16	0.0085	
X_3^2	0.0343	1	0.0343	0.1224	0.7495	
Residual	0.8404	3	0.2801			
Cor Total	40.57	12				
Adeq prec	12.46					
ANOVA for FFA Conversion						
Model	1172.75	9	130.31	15.74	0.0222	significant
X_1	122.38	1	122.38	14.79	0.0310	
X_2	605.35	1	605.35	73.14	0.0034	
X_3	25.35	1	25.35	3.06	0.1784	
X_{12}	1.61	1	1.61	0.1949	0.6888	
X_{13}	0.0240	1	0.0240	0.0029	0.9604	
X_{23}	0.0992	1	0.0992	0.0120	0.9197	
X_1^2	4.37	1	4.37	0.5278	0.5201	
X_2^2	315.17	1	315.17	38.08	0.0086	
X_3^2	1.04	1	1.04	0.1258	0.7463	
Residual	24.83	3	8.28			
Cor Total	1197.58	12				
Adeq prec	12.46					

The F-value of the model was 15.76, indicating that the model was significant. There was only 2.22% of noise potential, which could cause the model unsuccessful in predicting the value of the response variable (FFA conversion). The p-value was 0.022 (< 0.05), designating that the variables were significant to the model. In this study, the influential variables were A, B, and B^2. Table 6 also demonstrates the value of adeq precision. Adeq precision measures the signal ratio to the disturbance (noise), and its value is expected to be higher than 4. A ratio of 12.46 resulted in this work, denoted that the inputted signal was appropriate.

Validation of the model capability in predicting is necessary to ensure the accuracy of the model approach. Figure 3 shows the model validation by comparing the predicted result with the experimental data. Figure 3(a) demonstrates that the predictive value based on the model's calculation was close to the experimental data. It was indicated by the

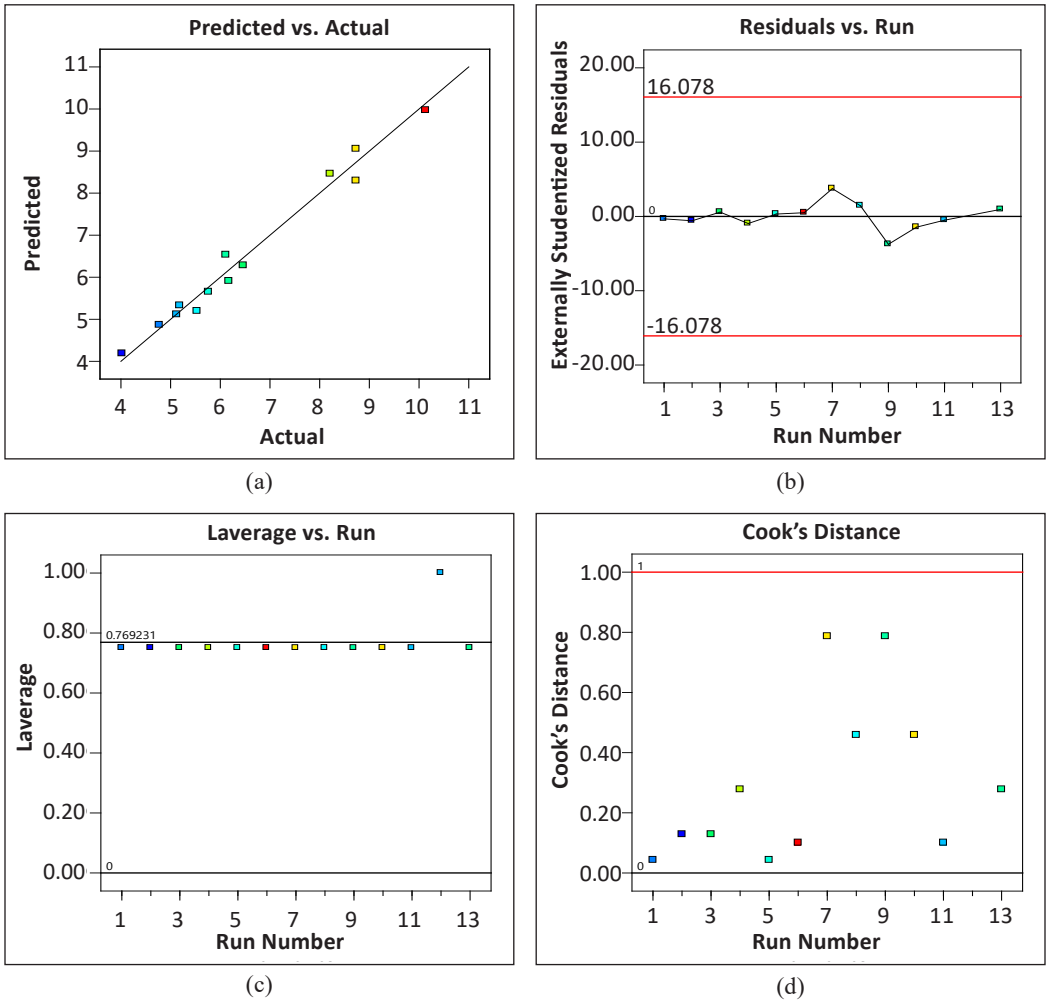
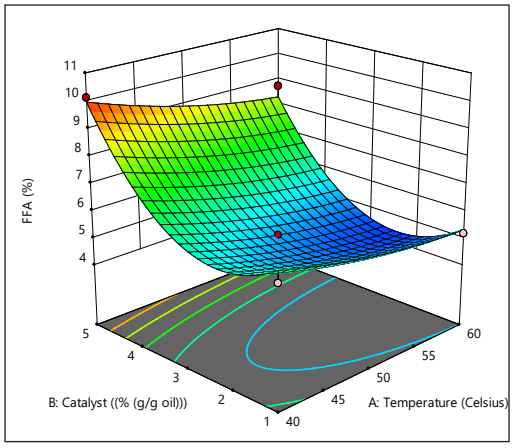


Figure 3. The Result of the Diagnoses for the Quadratic Model Approach

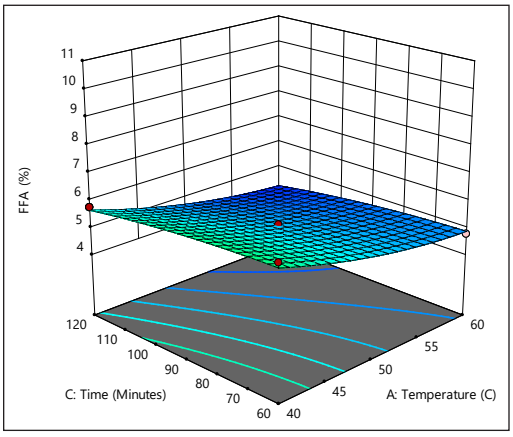
point of the prediction and experimental response values just about the 45° line. It specified that the proposed model was successfully identified the correlation of the input variables (catalyst concentration, reaction temperature, and reaction time) to the response (reaction conversion).

The model suitability was further determined by constructing a plot between the externally studied residuals and the prediction value. Figure 3(b) exhibits that all the data were under the limit, meaning that the model was suitable. As shown in Figure 3(c), all the leverage parameters were less than 1. It denoted that there was no significant error that could affect the model approach. Figure 3(d) presents that all the points were under the expected Cook's Distance Parameter. It implied that there is no significant error in observation in taking the experimental data. All the results of the model diagnoses demonstrated that the quadratic model developed in this analysis was appropriate for FFA content and FFA conversion optimisation in the FFA esterification using a sulfuric acid catalyst. The graphical illustration, termed response surface, is frequently used to justify the individual and cumulative influences of the experimental variables and their successive effect on the response (Liu et al., 2014).

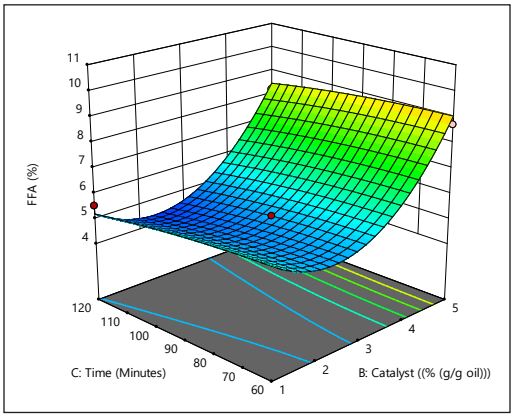
The significant variables affecting the FFA content and conversion were temperature and catalyst concentration as demonstrated in Figures 4 and 5. It can be observed that the FFA content reduced and, in contrast, the FFA conversion rose due to the temperature increase up to



(a)



(b)



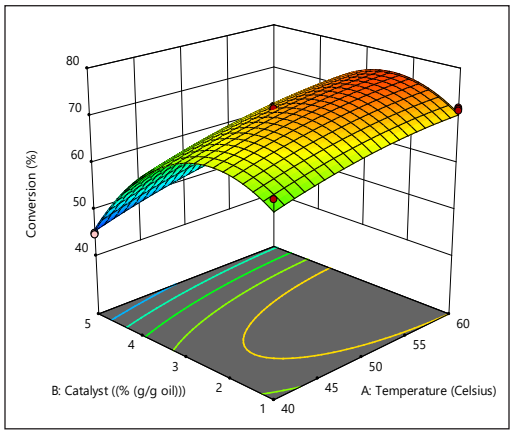
(c)

Figure 4. Three dimensional (3D) response surface of the effect of the process condition to the FFA content. (a) Reaction time = 90 min; (b) Catalyst concentration = 5 (g/g RNSO); and (c) Reaction temperature = 50°C.

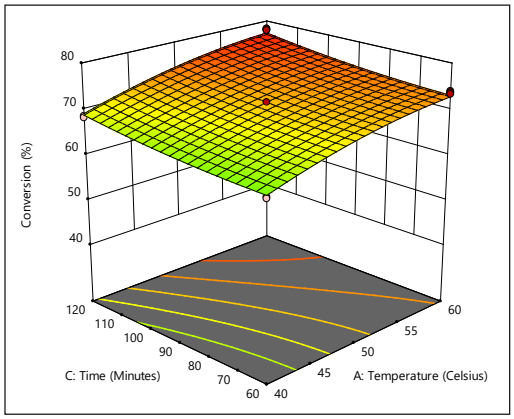
60°C. Additionally, increasing catalyst concentration from 1 to 3% significantly enhanced the FFA conversion and lowered the FFA content. However, an additional amount of catalyst employment did not result in the higher reaction conversion and the FFA removal. Reaction time considerably improved the reaction conversion and FFA removal from 0 to 60 minutes. After 60 minutes, reaction time slightly affected the esterification reaction.

In this work, the Derringer method was employed for the FFA conversion and FFA removal optimisation in the esterification using a sulfuric acid catalyst. In the complex system, various experimental variables have to be considered simultaneously to determine the optimum condition. It is known as a multi-response problem based on Multi-criteria Decision Making. In this case, the desirability approach is often employed as a vigorous instrument for optimisation in a multi-response system. The Derringer method is among the popular desirability method. The desirability function values are between 0 and 1. The value 0 means that the factors provided an undesired response. On the other hand, the value 1 indicates the optimal condition of the parameter evaluated (Amdoun et al., 2018).

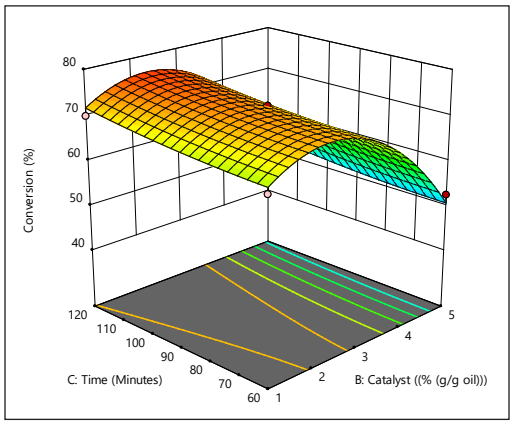
Based on the RSM simulation, it was revealed that the optimum conversion and the FFA content were 78.27% and 4%, respectively, achieved at the reaction temperature of 59.09 °C, catalyst concentration 1.98% g/g RNSO, and reaction time of 119.95 minutes. At this operation condition, the value of the desirability ramp



(a)



(b)



(c)

Figure 5. Three dimensional (3D) Response surface of the effect of the process condition to the FFA conversion. (a) Reaction time = 90 min; (b) Catalyst concentration = 5 (g/g RNSO); and (c) Reaction temperature = 50°C.

was 1 (Figure 6). The result fitted the experimental data and indicated the accuracy of the model. A similar method of optimisation applying desirability function was also described by (Mourabet et al., 2017).

Extrapolation was performed using RSM to predict the operating conditions and achieve a maximum of 2% FFA content. As shown in Figure 7, the FFA content can be lowered up to 2% with the reaction condition as follows: reaction temperature, catalyst concentration,

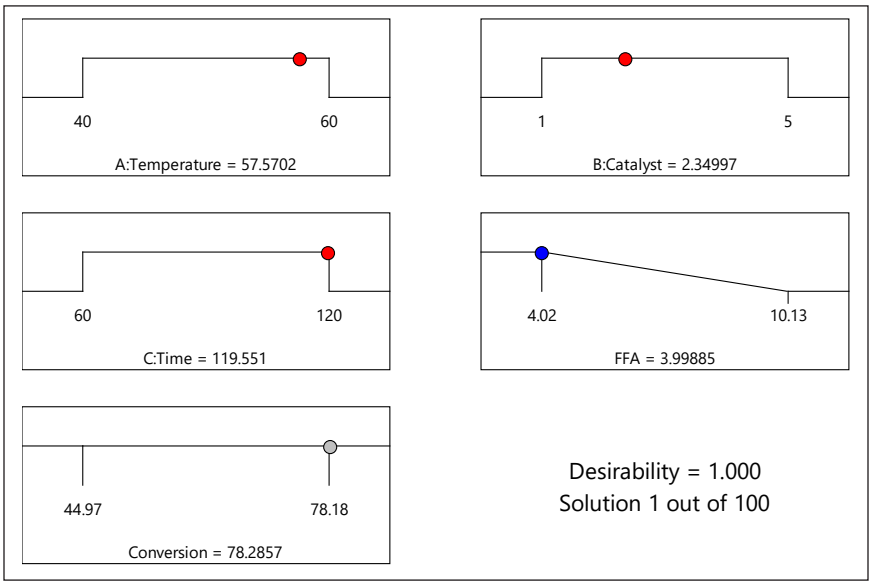


Figure 6. Optimisation of FFA conversion using RSM (Quadratic model)

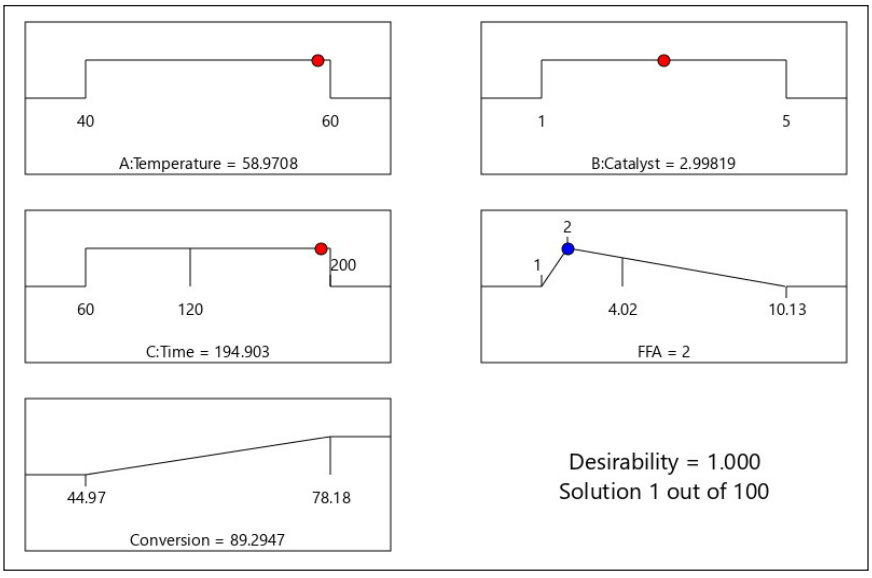


Figure 7. RSM prediction of operation condition on the FFA esterification using sulfuric acid catalyst to decrease the FFA content to 2%

and reaction time were 58.97°C, 3%, and 194.9 minutes, respectively, whereas the molar ratio of oil to methanol was fixed at 1:30. Therefore, the FFA conversion achieved was estimated at 89.3%.

The result has shown that RSM is simple and effective for process optimisation. Furthermore, the RSM and desirability function combination lead to the more accurate finding of the optimal condition. The identical deduction was reported by Amdoun et al. (2018). This study is significant in providing the optimum operating condition for reducing the FFA in CNSO to fulfil the allowable level of FFA content before being used as feedstock for biodiesel production via base catalysed transesterification reaction.

CONCLUSION

The experimental work of FFA esterification in RNSO with methanol in the presence of sulfuric acid catalyst has shown the optimal reaction condition at the reaction temperature of 60°C, a reaction time of 120 minutes, the molar ratio of RNSO) to methanol of 1:30, and the reaction times of 120 minutes, which yielded the reaction conversion of 78.18% and the FFA concentration of 4.01%. This value did not match the maximum acceptable FFA content value for alkaline catalysed transesterification (2%). The RSM was performed to estimate the optimal operation condition for achieving the FFA content of 2%. The RSM model analysis demonstrated that the quadratic model was the most suitable for optimising this process in future work. The RSM extrapolation predicted that the FFA content of 2% could be obtained at the reaction temperature, catalyst concentration, reaction time of 58.97°C, 3%, and 194.9 minutes, respectively, and the fixed molar ratio of oil to methanol of 1:30.

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