APPLICATION OF RESPONSE SURFACE METHODOLOGY TO OPTIMIZE BIODIESEL PRODUCTION FROM ESTERIFICATION OF PALMITIC ACID IN EXCESS METHANOL

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ABSTRACT

The main purpose of this study was to find out optimal conditions for producing biodiesel via esterification of palmitic acid in excess methanol using solid acid catalyst, viz. Amberlite™ IR-120 (H) resin. A stepwise regression for Box-Behnken design was performed to optimize parameters of this process. A 93.94 % of conversion efficiencies could be explained by an insignificant lack-of-fit response surface model ($R^2 = 0.9394$; $p = 0.259$). Optimum conditions were found as follows: 8:1 in the molar feed ratio of methanol to palmitic acid, a reaction temperature as 61.0 °C, a reaction time of 11.73 h. The catalyst loadings and agitation speed were kept constant at 10 wt.% of palmitic acid and 600 rpm, respectively. Under these conditions, conversion efficiency of palmitic acid to palmitic acid methyl ester reaction is (97.60 ± 0.64) %, and it is nearly 0.19 % difference between observed and predicted values. The solid catalyst can be reused at least five times after treating in a simple way.

Keywords: biodiesel, resin, methyl palmitate ester, Box-Behnken, stepwise regression.

1. INTRODUCTION

Economic development has consumed a lot of non-renewable energy resources particularly fossil fuels. Most of them have caused several problems for not only environment but also human health. Therefore, it is necessary to develop alternative energies, for example biodiesel, to replace non-renewable resources [1, 2].

Most homogeneous catalysts in biodiesel production have some disadvantages such as being difficult to separate or purify products, consuming more energy to remove neutralized water from reacted mixture [1, 3]. To overcome these drawbacks, solid catalysts would be of great interest for biodiesel production [1]. In this work, a strongly acidic cation exchange resin, Amberlite™ IR-120 (H) resin, as a solid catalyst was conducted to esterification reaction of palmitic acid in excess methanol. Methanol was used because of its advantages such as low price compared to other alcohols and physical-chemical properties [4].

Design of experiments (DOE) is usually applied to experimental science and engineering fields because of its advantages as reducing costs and time for experiments [5]. It begins with defining of a problem, choosing appropriate variables, gathering and interpreting of experimental results, fitting and optimizing the model [4, 6, 7]. Based on our previous results [8], stepwise technique was successfully applied to optimize parameters of biodiesel production via the first-order model. However, the first-order model could not well explain the difference between actual and predicted conversion efficiency at optimum area. Therefore, it is necessary to develop a quadratic model for our aims. In this lab-scale work, a stepwise regression of response surface methodology namely Box-Behnken design [6, 7] was employed to find out the optimal conditions of independent variables of the palmitate methyl ester reaction.

2. MATERIALS AND METHODS

2.1. Chemicals

Methyl alcohol anhydrous and palmitic acid (98 %), a product of Sigma-Aldrich®, were of analytical standard reagent. The catalyst namely Amberlite™ IR-120 (H) resin was pre-heated at 110 °C for 48 hours to remove water content. Then, it was put in a desiccator before transferring to the reactor.

2.2. Equipment and experiments

The experiments were performed in a three-neck flask connected to a thermometer, a flux condenser. The reactor was placed in a temperature controlled jacket, and put on a magnetic controlled machine [9]. The acid number of samples were record by a titrator namely Metrohm 887 Titrino.

Firstly, a suitable amount of palmitic acid and methanol was separately pre-heated to desired temperature before transferring to the three-neck reactor. Consequently, the catalyst was simultaneously added to the reactor for catalysing esterification to desired time. The acid number (mg KOH/g) at initial time (A_i) and the desired time (A_f) of samples were determined by auto-titration method. Finally, the conversion efficiency of reaction was calculated by using Eq. 1 [9, 10].

$$Conversion\ yield, \% = \frac{A_i - A_f}{A_i} \times 100. \quad (1)$$

3.3. Response surface methodology and statistical analysis

In some previous researches [4, 11], the important independent variables affected on the conversion of biodiesel production reaction were reaction temperature, molar ratio of reactants, reaction time, amount and concentration of catalyst, and reacted mixture stirring speed. However, our previous results [8] reported that the influences of two last factors were insignificant. Therefore, this work was focused on the three first parameters. Catalyst concentration and stirring speed were kept at 10 wt % (palmitic acid) and 600 rpm, respectively. In the same way of our previous research, the response was esterification conversion efficiency, Y (%). The uncoded and coded of the 3-level variable design were listed as table 1.

Table 1. The levels of parameters in coded and uncoded

Uncoded	*Coded*	*Factors*	*Levels*		
			Low (-)	*Centre (0)*	*High (+)*
U_1	X_1	The molar ratio of methanol and palmitic acid	7.0	8.0	9.0
U_2	X_2	Reaction temperature, °C	57.0	61.0	65 0
U_3	X_3	Reaction time, h	8.0	11.0	14 0

In this case, a three variables Box-Behnken design with three replicates at centre was carried out as response surface method (RSM) to find out an optimum condition of factors for a biodiesel production via esterification of palmitic acid (table 2).

Table 2. The Box-Behnken experimental design with three factors.

No.	*Pattern*	U_1	U_2	U_3	*Y, %*	$\hat{Y}$, %	*No.*	*Pattern*	U_1	U_2	U_3	*Y, %*	$\hat{Y}$, %
1	—0	7	57.0	11.0	94.47	94 85	9	−0−	7	61.0	8.0	95.92	96.00
2	—+0	7	65.0	11.0	96.13	95.43	10	+0−	9	61.0	8.0	95.85	96.00
3	+−0	9	57.0	11.0	95.65	95.42	11	−0+	7	61.0	14.0	95 76	96.10
4	++0	9	65.0	11.0	94.85	94.86	12	+0+	9	61.0	14.0	96.02	96.10
5	0—	8	57.0	8.0	94.59	95.78	13	000	8	61.0	11.0	97.45	97.50
6	0−+	8	57.0	14.0	96.95	96.27	14	000	8	61.0	11.0	97.86	97.50
7	0+−	8	65.0	8.0	95.91	96.18	15	000	8	61.0	11.0	97.93	97 50
8	0++	8	65.0	14.0	96.04	95.90							

The first twelve rows stood for midpoints of edges of the process space, and the three last ones are runs at the centre [6]. The postulated mathematical model was a quadratic equation, Eq.2. A JMP® software was used for fitting a response surface model and other analytical statistics. The formulation was produced and randomly performed to minimize error.

$$\hat{Y} = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j + \varepsilon \qquad (2)$$

where $\hat{Y}$, β_j, β_{ii}, β_{ij} and ε meant predicted response variable; linear, squared and cross-product coefficients; and the residual, respectively [6].

Based on our previous results [8], the stepwise technique was continued to apply for fitting the model because of its advantages. There are three popular selection methods of stepwise regression namely forward selection, backward elimination and stepwise iteration. Stepwise will generate a screen with recommended model terms checked and *p*-values shown [7]. In this investigation, the *p*-value setting of stepwise analysis was 0.25 to enter and 0.05 to leave the term out of the full model.

A canonical analysis was performed to definitely know where the global maximum of conversion in this design was and to determine the shape of the fitted response.

3. RESULTS AND DISCUSSION

3.1. Statistical analysis and fitting model

Figure 1 showed influence of the main effects with sensitivity indicator on reaction conversion whereas the optimal conditions were located around 8 : 1 of molar ratio between methanol and palmitic acid, 61 °C of reaction temperature and slightly higher than 11.0 h of reaction. That meant the setting conditions of experiments was overlapped the optimum area. This conclusion was also consistent with *p*-value for a linear model. In our case, a quadratic function should be better than the linear model in simulating results.

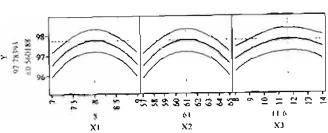

Figure 1. Main effects plot with 95 % confidence intervals.

Table 3. Parameter estimates after stepwise analysis of Box-Behnken design for biodiesel production

Term	*Estimate*	*Std. error*	*t ratio*	*Prob. > |t|*	*Term*	*Estimate*	*Std. error*	*t ratio*	*Prob. > |t|*
Intercept	97.75	0.232	421.9	1e-14*	X_2X_3	-0.558	0.201	-2.78	0.032*
X_1(7,9)	0.011	0.142	0 079	0.939	X_1X_1	-1.228	0.209	-5.88	0.001*
X_2(57,65)	0.159	0.142	1.119	0.306	X_2X_2	-1.243	0.209	-5.95	0.001*
X_3(8,14)	0.313	0.142	2.202	0.070	X_3X_3	-0.631	0.209	-3.02	0.023*
X_1X_2	-0.615	0.201	-3.06	0.022*					

After doing forward stepwise analysis on the data in table 2, a reduced model (second-order polynomial function) was attained as table 3 and Eq. 3.

At 5 % significant level, the significant factors that were stared should be gone into the reduced model. The important interaction effects were found between molar ratio of reactants and reaction temperature (X_1X_2), between reaction temperature and reaction time (X_2X_3). All squared terms of main factors were also significant. Although the three main effects were non-significant, they should be kept in the final model because of following the hierarchy principle [7].

$$\hat{Y}_R = 97.75 + 0.011X_1 + 0.159X_2 + 0.313X_3 - 0.615X_1X_2 - 0.558X_2X_3 - 1.228X_1^2 - 1.243X_2^2 - 0.631X_3^2 \quad (3)$$

(R^2 = 0.9394; Adjusted R^2 = 0.8586; Root Mean Square Error (RMSE) = 0.4013).

Contribution of individual effects was also figured out, figure 2 (left). In this case, the effects of X_1^2 and X_2^2 were the most important. Their contributions was approximately 30% while those of X_1 and X_1X_3 were nearly zero.

3.2. Checking model adequacy

The determine coefficient value, R^2, of 93.94 % meant that not only a good agreement between predicted and observed values but also the obtained mathematical model Eq. (3) could

predict the conversion efficiency of biodiesel very well [6], figure 2 (middle). Furthermore, the high adjusted determination coefficient, adjusted R^2 = 85.86 %, indicated a high significant of the model [6]. These results were consistent with *p*-values of model and lack-of-fit in analysis of variance (ANOVA, table 4) and lack-of-fit analysis (table 5) for the reduced model.

Table 4. Analysis of Variance (ANOVA).

Source	*df*	*SS*	*MS*	*F*	*p-value*
Model	8	14.984	1.873	11.630	0.0039
Error	6	0.966	0.161		
Total	14	15.950			

Table 5. Lack-of-fit analysis.

Source	*df*	*SS*	*MS*	*F*	*p-value*
Lack-of-Fit	4	0 832	0.208	3.093	0.259
Pure Error	2	0.134	0.067		
Total Error	6	0.966			

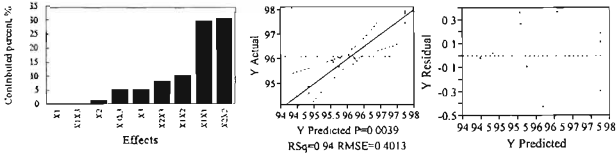

Figure 2. Contribution percentage of individual terms to R^2 value of the model (*left*); Actual by Predicted plot (*middle*) and Residual by Predicted plot (*right*).

Further, the adequacy of the model was tested with predicted and experimental values plot (*middle*) and residual plot (*right*) shown in figure 2. The red line was perfect fit with points corresponding to zero error between observed and predicted conversion (*middle*), and the points were symmetry of zero value of conversion residual (*right*). These results demonstrated that the fitted model was successful in capturing correlation between conversion efficiency and three selected independent variables.

3.3. Optimization for biodiesel production variables

The above results showed that the influences of three main factors were not important ($p > 0.05$). However, two interaction effects and three squared effects of main parameters were significant. Therefore, the next step is application of the developed regression model, *Eq. 3*, to optimize the three selected parameters to attain the highest conversion. These three independent variables were listed in table 1. The lowest conversion efficiency was obtained in run 1st while the highest one was assigned in run 15th, table 2.

The left and right contour plots looked like elliptical nature while the middle one was nearly the circular nature of the contour shape. It proved the interactions X_1X_2 and X_2X_3 were significant, and there was no interaction between X_1 and X_3 [12].

After doing Canonical and Ridge Analysis, it concludes that the surface was shaped like a hill; there was a unique optimum combination of factor values; the stationary point was within the region of exploration; the factors that were the predicted responses most sensitive were X_1 and X_2. Moreover, the stationary point of this design was located at coordinates of uncoded and

coded variables (8.01:1, 61.02 °C, 11.73 h), and (X_1 = 0.0114, X_2 = 0.0059 and X_3 = 0.2458), respectively. At these conditions, the response variable was maximal at 97.79 %.

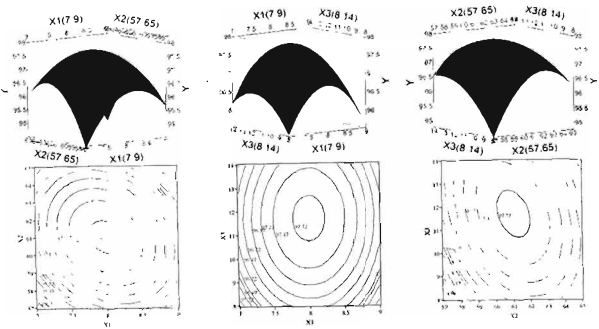

Figure 3. Surface and contour profiler for combination of ratio molar of reactants and reaction temperature (*left*); ratio molar of reactants and reaction time (*middle*); reaction temperature and reaction time (*right*).

Three confirmation experiments were conducted under these optimal conditions (U_1 = 8:1, U_2 = 61 °C and U_3 = 11.73 h) to verify the quadratic response surface model could satisfactorily describe the conversion or not. It revealed 0.19 % difference between observed and calculated values. Therefore, this model could be well applied to this case.

3.4. Recycling catalyst

The used catalyst was washed by using pure methanol. After drying at 110 °C for 48 h, it was ready for using in the next cycle. It was not statistically different after five cycles of experiment (table 4). This result also demonstrated that Amberlite™ IR-120 (H) resin was a stable catalyst.

Table 4. Recycling catalyst.

Cycle	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}
Conversion (*), %	90.10 ± 1.01	89.22 ± 0.93	90.12 ± 0.97	88.59 ± 1.10	89.71 ± 1.18

(*) *molar ratio of methanol : palmitic acid, reaction temperature, reaction time, catalyst loadings and stirring speed were 8:1, 60 °C, 5.0 h, 10 wt.% of palmitic acid and 600 rpm, respectively.*

4. CONCLUSIONS

Forward stepwise technique was successful to optimize the biodiesel production process via response surface methodology. These optimum conditions were at reaction temperature of 61 °C,

a methanol to palmitic acid molar ratio of 8:1, a reaction time of 11.73 h. Under these conditions, the maximum conversion yield was (97.60 ± 0.64)% obtained by experiment. It was not statistically different from 97.79 % that was calculated by using the developed model.

The Amberlite IR-120 (H) resin can be used as a solid acid catalyst for the esterification of palmitic acid in excess methanol.

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1.

TÓM TẮT

ỨNG DỤNG PHƯƠNG PHÁP MẶT MỤC TIÊU TỐI ƯU HÓA QUÁ TRÌNH ĐIỀU CHẾ NHIÊN LIỆU SINH HỌC TỪ ACID PALMITIC KHI CÓ DƯ METANOL

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Bài báo này trình bày các điều kiện tối ưu của quá trình sản xuất nhiên liệu sinh học thông qua phản ứng ester hóa acid palmitc trên nền xúc tác rắn, Amberlite™ IR-120 (H), khi có dư methanol. Các điều kiện tối ưu của quá trình như sau: tỷ lệ mol methanol/acid palmitic là 8/1, phản ứng được vận hành ở 61,0 °C, trong thời gian khoảng 11,73 giờ. Trong khi đó, liều lượng xúc tác và tốc độ khuấy trộn lần lượt được cố định tại 10 wt.% khối lượng của acid palmitic và 600 rpm. Hiệu suất ester hóa đạt được xấp xỉ (97,60 ± 0,64) %.

Từ khóa: biodiesel, resin, methyl palmitate ester, Box-Behnken, stepwise regression.