Optimization of Process Parameters for Alkaline-Catalysed Transesterification of Palm Oil Using Response Surface Methodology
(Pengoptimuman Parameter Proses untuk Transesterifikasi Minyak Sawit Bermangkin Alkali Menggunakan Kaedah Sambutan)

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ABSTRACT

Biodiesel (fatty acid methyl esters) was synthesized from direct transesterification of vegetable oils, where the corresponding triglycerides react with methanol in the presence of a suitable catalyst. The alkali catalysts are the most common catalyst used in biodiesel industry because the process proves faster and the reaction conditions are moderate compared to the acid catalyst. In the present study, biodiesel production using heterogeneous alkaline-catalysed transesterification process (KOH supported on SBA 15) was proposed. The influence of reaction temperature x_1 (50 - 90°C), ratio of methanol to oil, x_2 (6:1 – 14:1 mol/mol), amount of catalyst, x_3 (1 – 5wt.%), and reaction time, x_4 (2 - 6h) to the reaction was studied. These four conditions were studied using design of experiment (DOE), based on four-variable central composite design (CCD) with α = 2. The process variables were optimised using the Response Surface Methodology (RSM) in obtaining the maximum yield of biodiesel. This method was also applied to determine the significance and interaction of the variables affecting the biodiesel production. The biodiesel produced in the experiment was analysed by gas chromatography, which considered five major fatty acid methyl esters. The optimal conditions of response were found to be 70°C for reaction temperature, 11.6 wt/wt of ratio methanol to oil, 3.91wt.% of weight of catalyst and 5 h for reaction time with 93% of biodiesel yield for predicted value and 87.3% from experimental.

Keywords: Base catalyst; biodiesel; response surface methodology

ABSTRAK

Biodiesel telah disintesis daripada transesterifikasi langsung minyak sayuran yang melibatkan trigliserida bertindak balas dengan metanol dengan kehadiran mangkin yang sesuai. Mangkin beralkali adalah mangkin yang biasanya digunakan di dalam industri biodiesel kerana proses terbukti lebih cepat dan keadaan tindak balas sederhana berbanding dengan mangkin berasid. Dalam kajian ini, penghasilan biodiesel menggunakan proses transesterifikasi bermangkinkan heterogen beralkali (KOH disokong di atas SBA-15) telah dikaji. Kesan suhu tindak balas, x_1 (50 - 90°C), nisbah metanol kepada minyak, x_2 (6:1 – 14:1 mol/mol), berat mangkin, x_3 (1 – 5wt.%), dan masa, x_4 (2 - 6 h) terhadap tindak balas dikaji. Empat keadaan ini telah dikaji menggunakan reka bentuk eksperimen (DOE) berdasarkan kepada empat pembolehubah reka bentuk gabungan berpusat (CCD) dengan α = 2. Pembolehubah proses telah dioptimumkan menggunakan kaedah sambutan permukaan (RSM) dalam mendapatkan hasil biodiesel yang maksimum. Kaedah ini juga digunakan untuk menentukan kepentingan dan interaksi pembolehubah-pembolehubah yang mempengaruhi hasil biodiesel. Biodiesel yang dihasilkan telah dianalisis melalui kromatografi yang mengambilkira lima metil ester asid lemak utama. Keadaan optimum sambutan didapati pada suhu tindak balas 70°C, nisbah metanol kepada minyak 11.6 mol/mol, berat mangkin 3.91 wt.% dan 5 jam masa tindak balas dengan 93% hasil biodiesel keluaran untuk nilai jangkaan dan 87.3% daripada eksperimen.

Kata kunci: Biodiesel; kaedah sambutan permukaan; mangkin beralkali

INTRODUCTION

Due to environmental, green chemistry and economic concerns, current research trend in catalysis has been focused on the transformation of homogeneous catalytic system into heterogeneous systems. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages, most important being the application of easier working up procedures, the easy catalyst separation from the reaction mixture and the reduction of environment pollutants (Venkatesan et al. 2004). Besides that, the process of transesterification is affected by various factors depending upon the reaction condition used. Some of the effects are free fatty acid and moisture of the source of oil, type of oil, catalyst type and concentration, molar ratio of alcohol to oil, type of alcohol, reaction time and temperature, mixing intensity and effect of solvents (Lopez et al. 2005; Meher et al. 2004) The economic and environmental interest in using oil and fats are also involved in the production of biodiesel.

The objective of this study was to optimize process variables of transesterification. The process variables studied were reaction temperature, ratio of methanol to

oil, weight of catalyst and reaction time. RSM was applied to relate these four process variables with the response (biodiesel yield) and to find the optimal combination of process variables that would maximise the biodiesel yield. Otherwise, the purpose of this research was to present the feasibility and reliability of the DOE method on the optimisation of the process variables.

MATERIALS AND METHODS

RAW MATERIAL AND CHEMICALS

Refined cooking oil (*Vesawit*) was obtained from the market and stored at room temperature. Methanol and n-hexane were purchased from Merck. The pure standard such as methyl myristate, methyl palmitate, methyl oleate, methyl stearate, methyl linoleate and methyl heptadecanoate obtained from CLSTR were used as the reference standards and internal standards for GC analysis respectively.

TRANSESTERIFICATION REACTION

The transesterification reaction was following a method reported by Noiroj et al. (2008). It was carried out in a 500 mL three-necked glass flask equipped with a condenser to avoid methanol loss, and equipped with a stirrer and detector thermocouple. The flasks were kept in an oil bath. The reaction procedure is as follows. First, the calculated amount of catalyst was dispersed in methanol under magnetic stirring. Then, oil was added into the mixture and temperature was set to the desired value with appropriate stirring rate. After 6 h, the mixture was taken out and excess methanol was distilled off under vacuum. Then the sample was taken out from the reaction mixture and the catalyst was separated by centrifugation. After the removal of glycerol layer, the biodiesel was collected for chromatographic analysis.

ANALYTICAL METHODS FOR BIODIESEL PRODUCT

Reference materials and samples were analysed using a gas chromatograph, equipped with a capillary column (nucol, 50 m × 50 um × 53 mm) and a flame ionisation detector (FID). Helium was used as the carrier gas. The injector temperature was 220°C and the detector temperature was 250°C. The analysis of biodiesel for each sample was carried out by dissolving 100 mL of diluted sample (biodiesel sample and n-hexane) into 100 mL of internal standard solution (concentration = 1 g/L). This mixture (1 μL) was injected into the GC. The procedure was adapted from Liu et al. (2007).

DESIGN OF EXPERIMENTS

The experimental design as a function of the selected process variables was carried out using central composite rotatable design (CCRD). In order to obtain the required data, the range of values of each of the four variables was determined. Reaction temperature (*T*), ratio methanol-to-oil (*M*), weight of catalyst (*W*) and reaction time (*t*) were chosen for the independent variables. For four variables ($n = 4$) and five levels (low (-) and high (+)), the total number of experiments was 30 determined by the expression: 2^n ($2^4 = 16$ factorial points) + 2n (2 × 4 = 8 axial points) + 6 (center points: six replications) as given in Table 1. Biodiesel yield was selected as the response for the combination of the independent variables. Experimental runs were randomised to minimise the effects of unexpected variability in the observed responses (Montgomery 2001).

STATISTICAL ANALYSIS

A quadratic polynomial equation by central composite design was developed to predict the response as a function of independent variables and their interaction. In general, the response for the quadratic polynomials is described below:

$$Y = \beta_0 + \Sigma\beta_i x_i + \Sigma \beta_{ii} x_i^2 + \Sigma \Sigma\beta_{ij} x_{ij} x_j \qquad (1)$$

where y is the response (yield); β_0 is the intercept coefficient, β_i is the linear terms, β_{ii} is the squared terms and β_{ij} is the interaction terms, and x_i and x_j are the uncoded independent variables (Ghadge & Raheman 2006). Analysis of variance (ANOVA) was applied to estimate the effects of main variables and their potential interaction effects on the biodiesel yield.

RESULTS AND DISCUSSION

MODEL FITTING AND STATISTICAL ANALYSIS

Results obtained from the experiments (observed and predicted) are summarized in Table 1 and shown in Figure 1. The results developed a second order polynomial equation (in coded units) that could relate biodiesel yield to the parameters study. The following quadratic model was explained in equation 2.

$$Y = 76.68 + 8.79x_2 + 12.44x_3 + 9.06x_4 - 11.77x_1^2 - 4.98x_2^2 - 5.38x_3^2 - 2.78\ x_4^2 + 3.22x_1x_4 + 3.50x_3x_4 \qquad (2)$$

From the experimental design in Table 1, experimental results in Table 2 and equation (2), the second order response functions representing Y is the response for biodiesel yield, x_1 the coded value of variable temperature (*T*), x_2 the coded value of variable ratio methanol to oil (*M*), x_3 the coded value of variable weight of catalyst (*W*), and x_4 the coded value of variable reaction time (*t*). The closer the value of R^2 to unity, the better the empirical models fit the actual data. On the other hand, the smaller the value of R^2, the lesser will be the relevance of the dependent variables in the model in explaining the behaviour of variations (Cao et al. 2008). Thus, the predicted values match the observed values reasonably well, with R^2 of 0.94.

TABLE 1. Observed and predicted values of transesterification process

Design points	Point type	Coded independent variable levels				Yield, % (responses)	
		x_1 (T)	x_2 (M)	x_3 (W)	x_4 (t)	Experimental (Observed value)	Predicted value
1	Fact	60	8	2	3	30.5	28.4
2	Fact	80	8	2	3	22.1	22.0
3	Fact	60	12	2	3	41.1	46.0
4	Fact	80	12	2	3	36.4	39.6
5	Fact	60	8	4	3	44.5	45.9
6	Fact	80	8	4	3	40.4	39.4
7	Fact	60	12	4	3	58.3	63.4
8	Fact	80	12	4	3	55.5	57.0
9	Fact	60	8	2	5	27.8	32.7
10	Fact	80	8	2	5	35.7	39.1
11	Fact	60	12	2	5	41.5	50.3
12	Fact	80	12	2	5	65.6	56.7
13	Fact	60	8	4	5	70.9	65.0
14	Fact	80	8	4	5	65.6	71.4
15	Fact	60	12	4	5	78.7	82.6
16	Fact	80	12	4	5	83.5	89.0
17	Axial	50	10	3	4	27.3	29.6
18	Axial	90	10	3	4	39.5	29.6
19	Axial	70	6	3	4	38.6	39.2
20	Axial	70	14	3	4	82.5	74.3
21	Axial	70	10	1	4	33.5	30.3
22	Axial	70	10	5	4	84.4	80.0
23	Axial	70	10	3	2	50.1	47.4
24	Axial	70	10	3	6	88.6	83.7
25	Center	70	10	3	4	77.6	76.7
26	Center	70	10	3	4	76.6	76.7
27	Center	70	10	3	4	75.9	76.7
28	Center	70	10	3	4	68.0	76.7
29	Center	70	10	3	4	80.0	76.7
30	Center	70	10	3	4	82.0	76.7

TABLE 2. ANOVA analysis for the quadratic model

Source	SS	DF	MS	F Value	Prob > F	
Model	12337.29	9.00	1370.81	37.97	< 0.0001	Significant
Residual	722.03	20.00	36.10			
Lack of Fit	605.90	15.00	40.39	1.74	0.2815	Not significant
Pure Error	116.13	5.00	23.23			
Cor Total	13059.31	29.00				

Std. Dev.	6.0084		R-Squared	0.9447
Mean	56.7567		Adj R-Squared	0.9198
C.V.	10.5863		Pred R-Squared	0.8505
PRESS	1952.7909		Adeq Precision	19.3177

Statistical analysis obtained from the analysis of variance (ANOVA) for response surface reduced quadratic model is shown in Table 2. The value of "P>F" for models is less than 0.05, indicated that the model is significant which is desirable as it indicates that the terms in the model have a significant effect on the response. The value of P<0.0001 indicates that there is only a 0.01% chance that a "model F-value" this large could occur due to noise. Generally P-values lower than 0.01 indicate that the model is considered to be statistically significant at the 99% confidence level (Ravikumar et al. 2005). Values greater than 0.1000 indicate the model terms are not significant. In this case, M, W, t, T^2, M^2, W^2, t^2, Tt and Wt are significant model terms. The insignificant model terms

can be removed and may result in an improved model. The "Lack of Fit F-value" of 1.74 implies the Lack of Fit is not significant relative to the pure error. There is a 37.97% chance that a "Lack of Fit F-value" this large could occur due to noise. Insignificant lack of fit is good as sufficiently good model fitting is desirable.
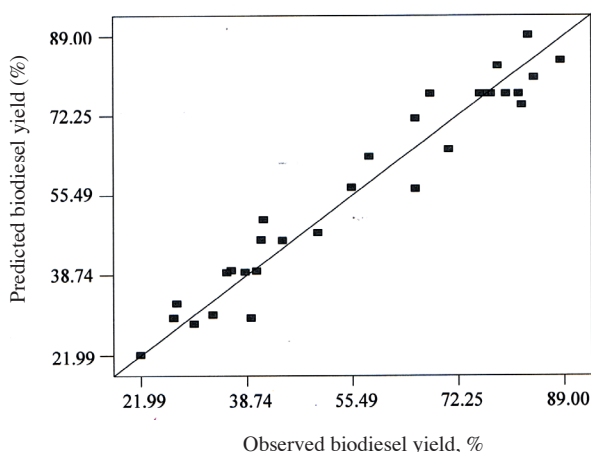

FIGURE 1. Relation between observed and predicted biodiesel yields

EFFECT OF PROCESS PARAMETERS

The effect of individual variables on the transesterification process was discussed by response surface one factor plot in Figure 2, while the interaction between variables is shown in Figure 3 in the form of three-dimensional response surface and contour plots.

INFLUENCE OF INDIVIDUAL EFFECT

The individual effect of A, B, and C towards biodiesel yield is plotted in the Figure 2. These three effects showed positive influence to the yield of biodiesel. The biodiesel yield increased with the increase of these three factors. This is due to the positive quadratic model as shown in equation 2. It also indicates that the experimental value must consider running effect of A, B and C at a higher level to maximize the biodiesel yield. However, the interaction factor also must be considered as the individual effect plot does not give information regarding the significant interaction involved.

INFLUENCE OF INTERACTION EFFECT

Three dimensional and countour plots for interaction effect of reaction temperature and reaction time towards biodiesel yield are shown in Figure 3. The biodiesel yield increased as the reaction time increased to its high level (5h). The biodiesel yield also increased with reaction temperature to its central level (70°C). Therefore, biodiesel yield decreased as the temperature increased towards its high level (80°C), and the stronger influence of reaction time occured when reaction time was at its high level. The decreasing of biodiesel yield at a higher reaction temperature was probably as a result of losing of methanol due to it did not condense effectively at a higher temperature as boiling point of methanol is 65°C.
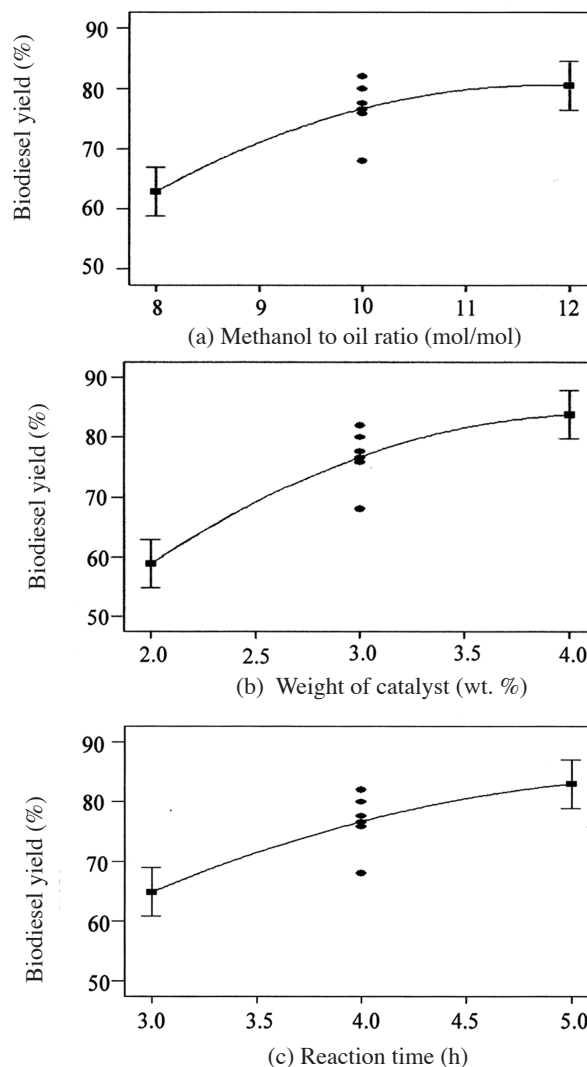

FIGURE 2. The individual effect of (a) ratio methanol to oil, (b) weight of catalyst and (c) reaction time towards biodiesel yield

CONCLUSION

The mathematical model developed could predict the biodiesel yield at any point in the experimental domain as well as the determination of the optimal biodiesel conditions. The high correlation in the model indicates that the second order polynomial model could be used to optimize the biodiesel yield. The conditions to get optimal response with 87.3% of biodiesel yield were found to be 70°C for the reaction temperature, 11.6 mol/mol for methanol to oil ratio, 3.91 wt.% for weight of catalyst and 5 h for reaction time. These results implicate that the optimization using a response surface methodology based on central composite design was a useful software in improving the optimization of biodiesel yield.
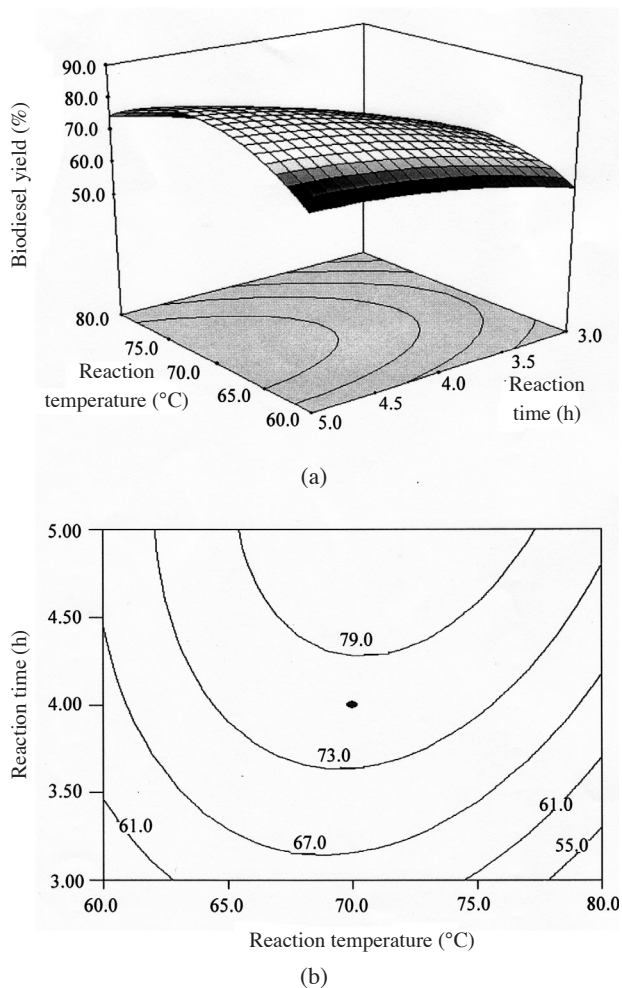
(a)

(b)

FIGURE 3. Three dimensional (a) and contour plot (b) for interaction for the effect of reaction temperature and reaction time towards biodiesel yield

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