Optimization of Conversion of Palm Fatty Acids Distillate into Biodiesel by using Response Surface Methodology

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ABSTRACT

High free fatty acid content in the Palm Fatty Acid Distilate (PFAD) potentially converted into Biodiesel by esterification process. The purpose of this investigation is to find the maximum free fatty acids (FFA) conversion in a PFAD by variation of process variables in FAME production using Amberlyst BD20 (type of cation-exchange resin) as heterogenous catalyst. Esterification reaction was carried out in 500 mL three-neck flat bottom flask and equipped by reflux-condenser sytem to protect methanol losses during the reaction take place. Conversion of free fatty acid was determined by evaluating the change of initial acid number (i.e 170 mg KOH/g sample) to its final value. A 3^4 full-factorial design experiment followed by Respon Surface Methodology (RSM) was applied for the determination of optimum condition: reaction temperature is 66.5789^oC, molar ratio Methanol to Oil is 6.6316 : 1, percent catalyst loading is 1.2763 %wt and stirrer speed is 260.5263 rpm to gives the maximum FFA conversion of 99.09% within 30 minutes. From this experiment also reported that the role of Amberlyst BD20 has a significant effect in converting high content of free fatty acid into biodiesel in a one-step reaction.

Keywords: *Esterification, PFAD, FFA Conversion, Biodiesel, Amberlyst BD20.*

1. INTRODUCTION

Biodiesel (Fatty Acids Methyl Ester) has become increasingly attractive worldwide because it is made from renewable resources which provide non-toxic fuel, biodegradable, less environmental impacts due to a better combustion; better lubricating effect on engines, non-sulfur emissions, non-particulate matter pollutants and higher flash point then finally does not contribute in global warming (Farag H. A., 2011). The main problems in the production and use of biodiesel are: to reduce the costs of production and to avoid the competition between the production of energy and food (Santacesaria E., et al., 2012). The costs of biodiesel production are highly dependent on the costs of feedstock which affect the cost of the finished product up to 60-75% (Yuan X., et al, 2008). To be more economically viable, using low-cost raw materials (unrefined oils) which generally contain high amounts of free fatty acids (FFAs) is a valuable alternative that would make their production costs more competitive than petroleum-derived fuel (Cardoso A. L. et. al., 2008). Therefore, recent biodiesel research count heavely on fatty acids-rich as a feedstock for biodiesel production to reduce the cost of its production. Palm Fatty Acids Distillate (PFAD) includes the type low-cost raw material that content above 93%wt of free fatty acids (FFA) and it is always produced as a waste from palm oil refining process. Since the high FFA level in the PFAD could result in soap formation which consumed the catalyst and reduced catalyst efficiency (Ma F and Hanna M. A., 1999), using type cation-exchange solid catalyst i.e Amberlyst BD20 was carried out in order to get maximum conversion of FFA with the present of Methanol. Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variation process (Sukjit T and Punsuvon V., 2013). The basic idea of this method is to utilize statistical-aided design of experiments to find the optimal value of a response. Through RSM, the number of experimental runs required is reduced then can generate sufficient information for a statistically acceptable result.

2. EXPERIMENTAL

2.1 Material

Palm Fatty Acids Distillate (PFAD) which content

93%wt FFA that is used in the research was obtained from Patum Vegetable Oil Co., Ltd, Thailand. The chemical compositions were: Palmitic acid 45.6, Oleic acid 33.3, Linoleic acid 7.7, Stearic acid 3.8, Myristic acid 1, tetracosenoic 0.6, Linolenic 0.3, Ecosanoic 0.3, Ecosenoic 0.2, and Palmitoleic 0.2 wt%. At room temperature PFAD is a light brown solid and melting to brown liquid on heating. Physical and chemical properties were: density 0.87 at 40°C, kin.viscosity 10.75 cSt at 40°C, Acid value is 170 mgKOH/gr, 0.05 %wt of Water content, Saponification number is 200.57 mgKOH/gr, and Iodine value is 57.57 gr I_2/100 gr. Amberlyst BD20 as solid catalyst was given by National Nanotechnology Center (NANOTECH), Thailand, while Methanol 99% was purchased from Chemical store around Bangkok, Thailand.

2.2 Esterification

Esterification reaction was carried out in 500 mL three-neck flat bottom flask and equipped by thermometer, hot plate-magnetic stirrer system, sampling device and reflux-condenser sytem to protect methanol losses during the reaction take place. The diagram of experimental set up for esterification process can be seen in Fig 1. Initially, reactor was charged with PFAD (in the solid phase), then it was heated to the selected temperature and PFAD already in the liquid phase. At the same time, but in another flask, certain amount of methanol was charged and heated. Once the selected temperature oil was achieved, the catalyst (Amberlyst BD20) and the hot methanol were added to the reactor under stirring and heating. The attainment of the selected temperature of the mixture determined the start of the reaction time. The system was mantained under the certan conditions during the reaction take place. Three milliliters of sample was taken every 5 minute and then was analyzed in order to determine the FFA conversion of PFAD. Percent of FFA conversion is defined as the ratio of change of 'acid value' of the reactor inlet and outlet stream to the inlet stream acid value.

$$\%FFA conversion = \frac{I_{Ain} - I_{Aout}}{I_{Ain}} \qquad (1)$$

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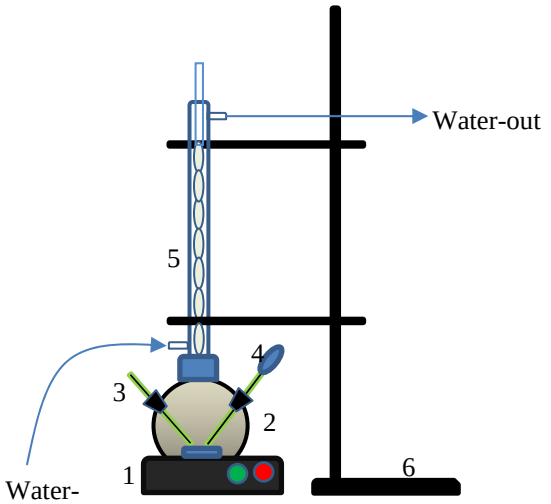


1. Hot plate-magnetic stirrer system
2. Three-neck flat bottom flask
3. Thermometer
4. Sampling device
5. Reflux condenser
6. Clamp and Statif

Fig 1. *Diagram of Esterification Equipment.*

3. DESIGN OF EXPERIMENT

The experiment has performed according to three-level full factorial design (3^k) and response surface methodology (RSM). It is intended to understand the relationship between factors (Reaction temperature, Molar ratio oil to methanol, Stirrer speed, and percent of catalyst loading) and Fatty Acids Conversion into Biodiesel, and also to determine the optimum conditions for production of biodiesel from PFAD. The range and levels of the investigated variables are listed in Table 1 as below.

Table 1 *Experimental range and levels of the independent variables.*

Variables	symbol coded	Range and Levels		
		-1	0	+1
Temperature (^oC)	X_1	55	65	75
Methanol/Oil molar ratio	X_2	1:6	1:9	1:12
Catalyst loading (%)	X_3	1	3	5
Stirrer speed (rpm)	X_4	250	300	350

A 3^4 full factorial design (81 runs of experiment) was applied with the central value (zero level) chosen for experimental design were: temperature = 65 ^oC, methanol/oil molar ratio = 1:9, catalyst loading = 3% of weight of oil and stirrer speed = 300 rotations per minute. The SPSS 20 software was used to find a model by doing multivariable regression and Matlab for graphical analyses and optimization of the model. The maximum values of FFA conversion in each run were taken as the response of the design experiment. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). Once the experiments are performed, the response variable (FFA conversion) was fitted a second-order model in order to correlate the response variable to the independent variable. The general form of the second-order polynomial equation is as follow:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + e \qquad (2)$$

Where i and j are the linear and quadratic coefficients, respectively, β is the regression coefficient, k is a number of factor (variable) studied and optimized in the experiment and e is a random error.

4. RESULT AND DISCUSSION

Free fatty acids conversions were found as shown as in table 2 as follow.

Table 2*. Three-level, full-factorial experiment matrix of four variables in coded and natural unit along with the observed responses (cont.).*

Run	X_1	X_2	X_3	X_4	FFA Conv (%)	Run	X_1	X_2	X_3	X_4	FFA Conv (%)
1	-1	-1	-1	-1	69.50	32	0	-1	0	0	97.65
2	-1	-1	-1	0	75.25	33	0	-1	0	+1	95.33
3	-1	-1	-1	+1	74.92	34	0	-1	+1	-1	95.65
4	-1	-1	0	-1	79.75	35	0	-1	+1	0	99.47
5	-1	-1	0	0	82.52	36	0	-1	+1	+1	98.65
6	-1	-1	0	+1	81.75	37	0	0	-1	-1	91.23
7	-1	-1	+1	-1	82.55	38	0	0	-1	0	95.71
8	-1	-1	+1	0	88.49	39	0	0	-1	+1	92.78
9	-1	-1	+1	+1	87.49	40	0	0	0	-1	93.54
10	-1	0	-1	-1	77.76	41	0	0	0	0	98.50
11	-1	0	-1	0	80.47	42	0	0	0	+1	96.78
12	-1	0	-1	+1	79.29	43	0	0	+1	-1	95.78
13	-1	0	0	-1	82.25	44	0	0	+1	0	97.65
14	-1	0	0	0	84.93	45	0	0	+1	+1	96.75
15	-1	0	0	+1	83.95	46	0	+1	-1	-1	94.92
16	-1	0	+1	-1	84.85	47	0	+1	-1	0	97.87
17	-1	0	+1	0	89.71	48	0	+1	-1	+1	96.28
18	-1	0	+1	+1	89.71	49	0	+1	0	-1	95.87
19	-1	+1	-1	-1	85.65	50	0	+1	0	0	99.65
20	-1	+1	-1	0	88.75	51	0	+1	0	+1	94.25

Table 2*. Three-level, full-factorial experiment matrix of four variables in coded and natural unit along with the observed responses.*

Run	X1	X2	X3	X4	FFA Conv (%)	Run	X1	X2	X3	X4	FFA Conv (%)
21	-1	+1	-1	+1	85.00	52	0	+1	+1	-1	97.65
22	-1	+1	0	-1	88.25	53	0	+1	+1	0	99.65
23	-1	+1	0	0	89.85	54	0	+1	+1	+1	98.25
24	-1	+1	0	+1	90.55	55	+1	-1	-1	-1	91.77
25	-1	+1	+1	-1	91.65	56	+1	-1	-1	0	95.78
26	-1	+1	+1	0	93.33	57	+1	-1	-1	+1	94.55
27	-1	+1	+1	+1	90.65	58	+1	-1	0	-1	93.28
28	0	-1	-1	-1	89.65	59	+1	-1	0	0	96.65
29	0	-1	-1	0	91.65	60	+1	-1	0	+1	95.95
30	0	-1	-1	+1	95.23	61	+1	-1	+1	-1	91.91
31	0	-1	0	-1	93.55	62	+1	-1	+1	0	92.65
63	+1	-1	+1	+1	95.77	73	+1	+1	-1	-1	89.21
64	+1	0	-1	-1	90.92	74	+1	+1	-1	0	91.62
65	+1	0	-1	0	91.97	75	+1	+1	-1	+1	86.47
66	+1	0	-1	+1	89.76	76	+1	+1	0	-1	87.42
67	+1	0	0	-1	90.47	77	+1	+1	0	0	88.87
68	+1	0	0	0	93.85	78	+1	+1	0	+1	87.29
69	+1	0	0	+1	90.95	79	+1	+1	+1	-1	85.44
70	+1	0	+1	-1	90.44	80	+1	+1	+1	0	87.23
71	+1	0	+1	0	90.86	81	+1	+1	+1	+1	84.47
72	+1	0	+1	+1	90.86						

By multiple regression and multivariable optimization method, it was obtained second-order polynomial equation as follow.

$$X = -517.542 + 13.344\,X_1 + 12.716\,X_2 + 32.386\,X_3 + 0.646\,X_4 - 0.082\,X_1^2 + 0.02\,X_2^2 - 1.296\,X_3^2 - 0.001\,X_4^2 - 0.156\,X_1X_2 - 0.346.X_1X_3 - 0.001\,X_1X_4 - 0.563\,X_2X_3 - 0.006\,X_2X_4 + 0.002\,X_3X_4 \quad (3)$$

Table 3 *Model Summary*

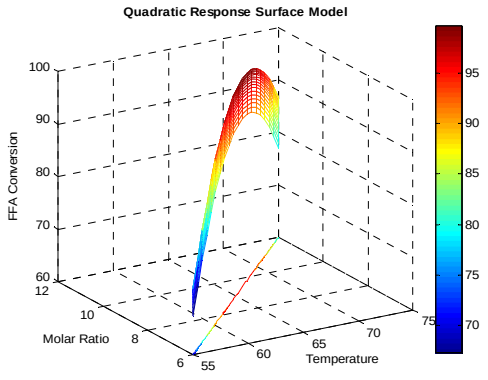
Model	R	R^2	Adjusted R^2	Std. error of the estimate
Eq. (3)	0.988	0.977	0.972	1.05096

This regression model was tested using analysis of variance for residuals minimization and revealed that the predicted response model was statistically significant. To test the fit of model, the regression equation and determination coefficient (R^2) were evaluated. In this case, the value of determination coefficient (R^2 = 0.977) indicates that the sample variation of 97.7% of FFA conversion is attributed to the independent variables and only 2.3% of total variations are not explained by the model. Adjusted (R^2 = 0.972) is also very high to advocate for a high significance of the model. The results of the second order response surface model fitting in the form of ANOVA are given in Table 4 as follow.

Table 4 *Analysis of variance (ANOVA) for the quadratic regression.*

Model		Sum of squares	Df	Mean Square	*F*	Sig.
Eq. (3)	Regression	3068.924	14	219.209	198.467	0.0001
	Residual	72.898	66	1.105		
	Total	3141.822	80			

The 3D response surface plots are generally the graphical representation of the regression equation were shown in Fig 2. (a), (b), (c), (d), (e) and (f), they are surface plot showing the optimal condition between independent variables in different fixed parameters.



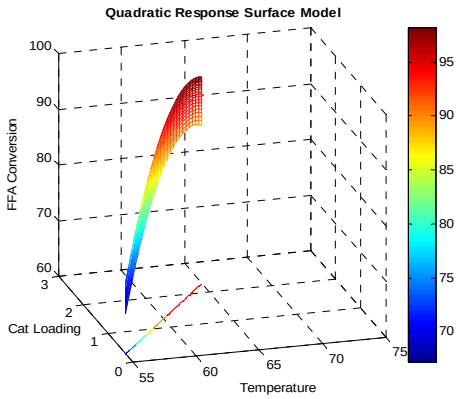
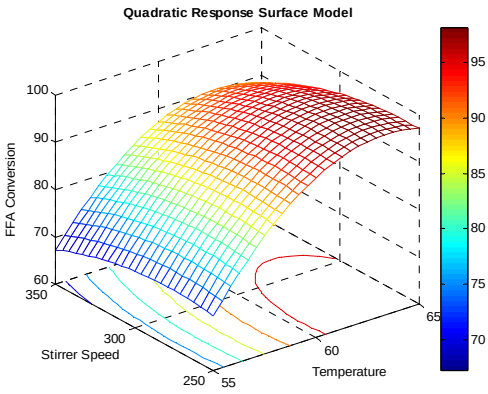
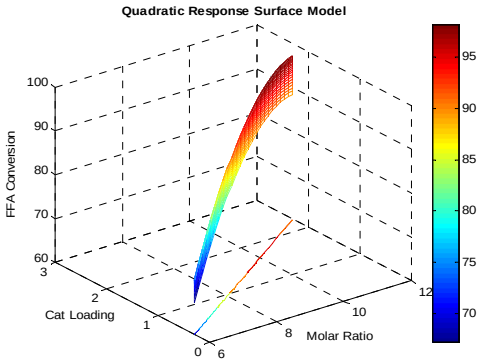


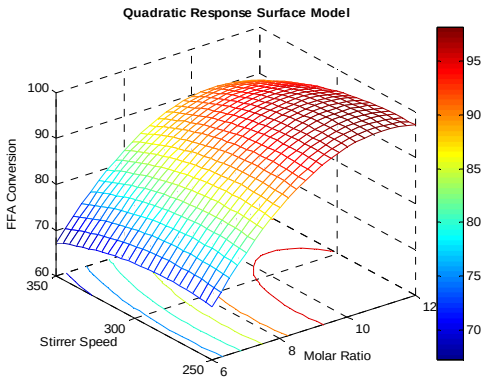
Fig. 2.4 (a) (b)



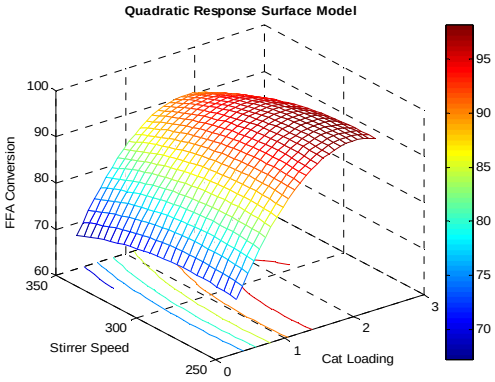
(c)



(d)



(e)



(f)

The optimal value of each independent variable was found as follow; reaction temperature is $66.5789\,^{o}C$, molar ratio oil to methanol is $6.6316:1$, percent catalyst loading is 1.2763 % and stirrer speed is

$260.5263\,rpm$, this would yield maximum FFA conversion is 99.59%.

5. ACKNOWLEDGEMENT

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