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OPTIMIZING ACID PRE-TREATMENT PROCESS OF CITRUS SEED OIL USING RESPONSE SURFACE METHODOLOGY

[1]Azhari and [2]Robiah Yunus

[1]Jurusan Teknik Kimia, Fakultas Teknik, Universitas Malikussaleh, Lhokseumawe, Indonesia

[2]Institute of Advanced Technology, Universiti Putra Malaysia, Serdang, Selangor Darul Ehsan, Malaysia

Email: armuh@yahoo.com Tel: +6285362159499

ABSTRAK

Proses esterifikasi dengan menggunakan katalis asam untuk menurunkan kadar asam lemak bebas di dalam minyak biji citrus dilakukan. Kadar asam lemak bebas dalam suatu minyak merupakan faktor penting yang perlu dipertimbangkan sebelum minyak dipilih sebagai bahan baku biodiesel yang diolah memakai teknik transesterifikasi dalam suasana berkatalis basa. Kadar asam lemak bebas minyak citrus harus kurang dari 1% untuk menghindari terjadinya reaksi pembentukan sabun. Untuk menghasilkan minyak citrus yang rendah kadar asam lemak bebas, maka perlu dilakukan proses esterifikasi dengan melibatkan beberapa parameter yang berpengaruh seperti: nisbah methanol dengan minyak citrus (%volum), jumlah katalis (%berat) dan waktu reaksi (menit). Metode RSM dipakai untuk mengoptimalisasi parameter reaksi. Kadar asam lemak bebas minyak citrus setelah diproses secara esterifikasi adalah 0.52% dan telah memenuhi syarat sebagai bahan baku untuk proses transesterifikasi pada kondisi parameter yang optimal yaitu: rasio metanol dengan minyak (48%volum), berat katalis (0.92%berat) dan waktu reaksi 112 menit. Seluruh ekperimen dilakukan pada kondisi suhu optimum yaitu 60°C.

ABSTRACT

Acid pre-treatment process of citrus seed oil is investigated to reduce free fatty acid (FFA) content of oil so that it could be used as feedstock of transesterification. The FFA content of oil is an important thing which should be taken into account in selecting a biodiesel feedstock when transesterification in the presence of alkali catalyst is used as the method. To avoid a soap formation during the reaction takes place, the oil FFA content must be < 1.0%. In this study, the high FFA content of citrus oil is used as the feedstock. The Response Surface Methodology (RSM) is applied to optimize the reaction parameters such as ratio of methanol to oil, percentage of catalyst loading, and reaction time. The optimized effecting parameters are as follows: reaction time, 112 min; percentage of catalyst, 0.92%w/w; and ratio of methanol to oil, 48%v/v. All experimental works are performed at fixed reaction temperature of 60°C. The results show that the treated oil is successfully applied as the alkali catalyzed transesterification feedstock. The final FFA level of citrus seed oil is 0.52%.

***Keywords**: Acid pre-treatment, Citrus seed oil, Response surface methodology*

INTRODUCTION

The lack of fossil oil reserved and environmental problem encourage the researchers to look for alternative sources of fuel. Edible and non edible oils have been investigated as the feedstock of biodiesel. Most of research findings prove that biodiesel is a good substitute for fossil based diesel in compression ignition engines due to it meets international standards for automotive use (Ma & Hanna 1999). Currently, oil from various plant seed or animal fat is produced in large quantities for using as transesterification based stock. The high content of impurities (FFA and moisture) results in the fresh oil needs acid pre-treatment step of process. Without carrying out such the treatment, the oil definitely cannot be used as the feedstock of transesterification in the presence of alcohol and alkali catalyst. Kulkarni and Dalai (2006) reported that transesterification of high FFA feedstock causes an undesired saponification reaction. The successful transesterification requires the high quality feedstock with the low content of impurities, in particular the FFA level of oil should be less than 1.0%.

Response surface methodology (RSM) is a useful statistical technique for optimizing experimental conditions and investigation of critical processes by reducing the numbers of experimental trials (Myers & Montgomery 2002). The optimization of a process by RSM is a faster and more economical technique for gathering research results than classical one-variable at-a-time or full-factorial experimentation. RSM was utilized to simultaneously relate these three variables with the aim of maximizing the response i.e. the reduction of FFA (%). Response surface methodology has been successfully applied to optimize transesterification reaction (Gwi-Taek et al. 2009; Umer et al. 2011; Giovanilton et al. 2011; Ahmad et al. 2009).

The purpose of this work is to carry out the acid pre-treatment process for citrus seed oil as biodiesel feedstock. The effect variables based on the RSM results such as percentage of catalyst loading (0.60, 0.68, 0.80, 0.92 and 1.00 %w/w), reaction time (80, 88.11, 100, 111.89, and 120 min) and volume ratio of methanol to oil (40, 42.03, 45, 47.97, and 50 % v/v) are selected in this work. Based on the previous study (Azhari et al. 2008), the entire experimental works are run under optimized reaction temperature i.e. 60°C. The reaction product is the treated vegetable oil with the lowest value of FFA (%) which is able to tolerate as the feedstock of transesterification.

METHODOLOGY

Materials and Equipments

The crude citrus seed oil with initial FFA of 6.15% is utilized as the feedstock. The chemicals employed are methanol (99.8% purity), sulphuric acid (95-98% purity), IPA (99.7% purity), phenolphthalein (1%), and potassium hydroxide (85% purity). The equipments used are three neck flask, graham condenser, thermometer, hot plate completed with magnetic stirrer, burette, and other glass wares.

Method of acid pre-treatment

The pre-treatment process is performed as follows: Initially, the fresh citrus seed oil is heated in the three necks flask until temperature reach about 60°C. The prepared catalyst is poured into reactor simultaneously with methanol at various concentrations as specified previously. Once the reaction has completed, the product is allowed into separation funnel to settle down for 2 h and the methanol water fraction at the top layer is removed. The treated oil is further analyzed on its final value of FFA through acid base titration.

Technique of Acid Base Titration

FFA content of the oils is determined using acid base titration technique (1). A standard solution of 0.1N potassium hydroxide solution is employed. The titration method is as follows. The neutralized IPA is prepared by placing 50 ml of IPA in a flask and carrying the solution to boil on a heating plate. Add about 0.5 ml of phenolphthalein and neutralized by drop-wise addition of 0.1N potassium hydroxide till a faint, but permanent pink colour is obtained. To prepare sample for analysis, weigh the specified amount of sample into a flask. In this study, the sample weight is 2.5 g. Add 50 ml of the neutralized solvent. Place the flask on the hot source and regulate the temperature to about 40°C. Shake the sample gently while titrating with standard alkali to the first permanent colour. The colour must persist for 30 seconds (Lin et al. 1995).

$$FFA(\%) = \frac{28.2 \times N \times V}{W} \quad (1)$$

where N, V and W denote normality of potassium hydroxide solution, volume of potassium hydroxide solution used in ml, and weight of vegetable oil sample.

Experimental design

The CCRD experimental design for the series of parameters employed in this study (acid pre-treatment process) is built by RSM with five level-three factor requires twenty runs of experiment (Myers & Montgomery 2002). The parameters selected are ratio of methanol to vegetable oils, A, in the range of 40-50 % v/v; percentage of catalyst loading, B, in the range of 0.6-1.0 wt%; and reaction time, C, in the range of 80-120 min. The remaining percentage of FFA in the treated oil (Y) is chosen to be the response variable. Each factor in this work is coded into level $-\alpha$, -1, 0, +1 and $+\alpha$ as shown in Table 1. The experimental design employed together with the results is given in Table 3.

Table 1 Factors and Levels for Central Composite Design

Parameters	Symbol	Coded Factor Levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Ratio of methanol (% v/v)	A	42.03	40	45	50	47.97
Percentage of catalyst (% w/w)	B	0.68	0.60	0.80	1.00	0.92
Reaction time (min)	C	88.11	80	100	120	111.89

Statistical analysis

In order to study the effect of reaction time, percentage of catalyst loading and ratio of methanol on the reduction of FFA percentage in the vegetable oils. The experimental data is analyzed via response surface methodology and fit to follow the second order polynomial equation. Second order coefficients are generated via regression. The response is initially fitted to the factors via multiple regressions. The quality of the fit of the model is evaluated using the coefficients of determination and analysis of variance. The quadratic response surface model is fitted to the following equation.

$$Y = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ij} x_i^2 + \sum_{i}^{k} \sum_{j}^{k} b_{ij} x_i x_j \quad (2)$$

Where Y is the response (the remaining percentage of FFA in the treated oil) variables, i and j are the linier and quadratic coefficients, b represents regression coefficient, k is the number of factors studied and optimized in the present study

Table 3 Experimental Design for the FFA concentration of *Citrus* Seed Oil

Standard order	Ratio of methanol (% v/v)	Catalyst concentration (%)	Reaction time (min)	Observed FFA *Citrus* seed oil
1	42	0.68	88	2.56
2	48	0.68	88	1.73
3	42	0.92	88	2.40
4	48	0.92	88	1.27
5	42	0.68	112	1.63
6	48	0.68	112	1.37
7	42	0.92	112	1.29
8	48	0.92	112	0.52
9	40	0.80	100	2.62
10	50	0.80	100	1.29
11	45	0.60	100	1.83
12	45	1.00	100	1.09
13	45	0.80	80	2.64
14	45	0.80	120	1.19
15	45	0.80	100	1.23
16	45	0.80	100	1.18
17	45	0.80	100	1.22
18	45	0.80	100	1.24
19	45	0.80	100	1.22
20	45	0.80	100	1.21

Values are mean ± SD

Table 4 Analysis of Variance (ANOVA) for Response Surface Quadratic Model (*Citrus* seed oil)

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	6.35	9	0.71	43.86	< 0.0001
A-Ratio of Methanol	2.00	1	2.00	124.45	< 0.0001
B-Percentage of Catalyst	0.68	1	0.68	42.50	< 0.0001
C-Reaction Time	2.29	1	2.29	142.28	< 0.0001
AB	0.082	1	0.082	5.10	0.0475
AC	0.11	1	0.11	6.73	0.0268
BC	0.041	1	0.041	2.53	0.1430
A^2	0.67	1	0.67	41.75	< 0.0001
B^2	0.024	1	0.024	1.49	0.2500
C^2	0.59	1	0.59	36.46	0.0001
Residual	0.16	10	0.016		
Lack of Fit	0.16	5	0.032	74.35	0.0001
Pure Error	0.00213	5	0.000427		
Total	6.51	19			

C.V = 8.25 % R^2= 0.9753 adj R^2= 0.9531 (*Citrus* seed oil)

RESULTS AND DISCUSSION

Pre-treatment process

Investigating the pre-treatment process to reduce the FFA concentration of citrus seed oil is carried out. The effect of each parameters and the interactions amongst of which is also studied. The reaction of pre-treatment which involves in this process is taking place under atmospheric condition.

Optimization of reaction condition by response surface methodoly

In this study, the process of FFA concentration reduction in vegetable oils which corresponds to the three parameters (ratio of methanol, percentage of catalyst loading and reaction time) is evaluated by employing RSM. Table 3 shows the result of experimental work of CCRD at each point. Twenty experimental works are performed in triplicate. Analysis of regression is utilized to fit the emperical model with the generated response variable data (Mason et al. 1989). The response variable (Table 3) is correlated with the three independent parameters using the polynomial equation (Eq. 2).

The observed and predicted values of the remaining percentage of FFA in the treated oils at the designed points of different pre-treatment reaction condition as shown in Figure 1. The lowest percentage of FFA concentration (0.52%) is obtained at 48 %v/v ratio of methanol, 0.92%w/w catalyst loading, and 112 min reaction time.

A Design-Expert 8 software (Stat-Ease, Inc. Minneapolis, USA) is employed to determine and evaluate the coefficient of full regression model equation and their statistical significance. Models are analyzed and validated by analysis of variance (ANOVA). The model appears to be adequate for observed data at 95% confidence level and p values < 0.05.

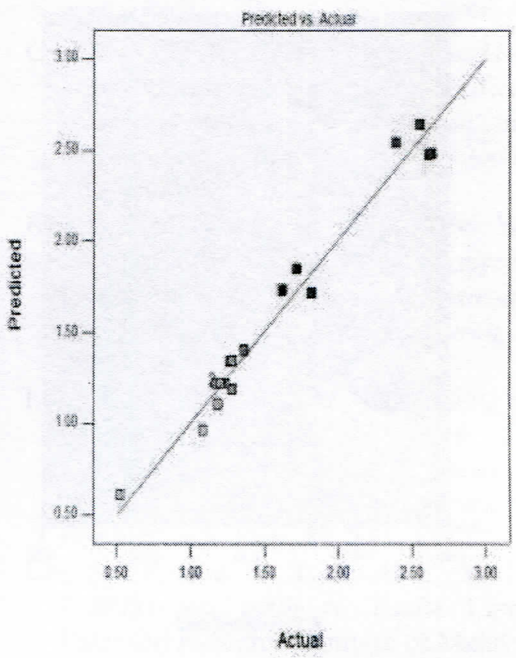

Figure 1: Plot of actual vs. predicted values

As the obtained data are analyzed using ANOVA (Table 4), the 95% confidence level, the model is found significance as computed F value (F_{model} = 43.86) with very low probability value (P value < 0.0001) indicates the high significance of fitted model showing the reliability of the regression model for predicting the remaining percentage of FFA in the treated oils (Lee et al. 2005).

FFA reduction of citrus seed oil

To investigate the characteristic of pre-treatment process in the presence of mineral acid, the high FFA oil must be provided. Important variables affecting the FFA concentration reduction in the pre-treatment process are the reaction time, ratio of methanol, and the percentage of catalyst

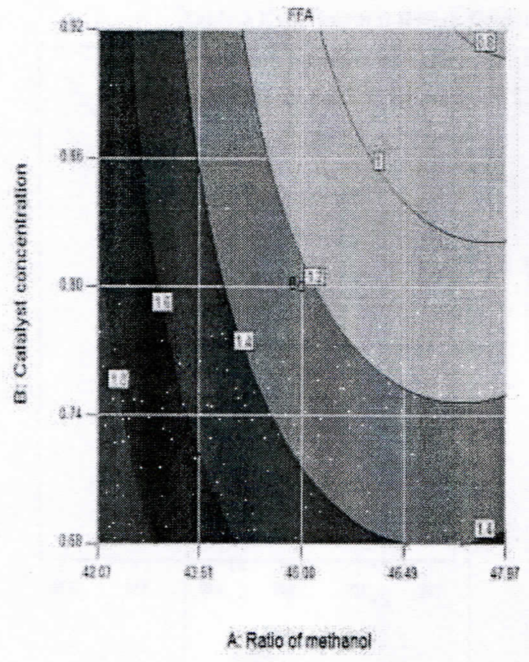

Figure 2: Surface plots of FFA concentration

loading. The pre-treatment process takes place under 60°C as the optimized reaction temperature. The effect of percentage of catalyst loading, previous study (Ghadge and Raheman 2005) reported that the reduction of FFA concentration in vegetable oils w affected by the amount catalyst loading. Th present study indicated that the symptom c FFA concentration reduction follows the tren of increasing reactant volume (methanol) an catalyst percentage until the optimu condition (0.9%w/w of catalyst) is reached shown in Figure 2.

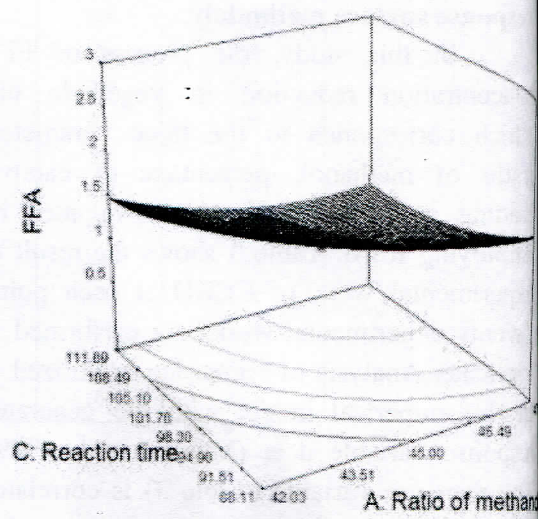

Figure 3: Contour plots of FFA concentration

The increasing of methanol concentration on the reduction of FFA percentage in citrus seed oil showed that the ratio of methanol is one of important variables effecting in pre-treatment process. Figure 2 shows that the reduction of FFA concentration is proportional to the intercalation of methanol ratio. At 45%v/v of methanol ratio, the FFA concentration drops to 1.2%. As the ratio of methanol increases more than 47%v/v, the FFA concentration of citrus seed oil encounters significantly subtraction to < 1.0% (Figure 3). However, the optimum ratio of methanol in this study is 48%v/v. The similar work reported that the optimum condition of pre-treatment of Jatropha curcas oil with sulphuric acid required 60%v/v methanol ratio (Azhari et al. 2008).

The reduction of FFA concentration i vegetable oil depends clearly on the tim span of reaction. Even though othe parameters played important roles i alleviating the FFA concentration, the pre treatment reaction time seems to have considerable effect on the final FF concentration as shown in Figure 3. Fro this figure, it is observed that the FF concentration in vegetable oils alleviate with increasing reaction time. The FF concentration reduced sharply less tha 1.0% at 112 min of reaction time. As th similar study (Riccardo et al. 2010) reporte that the optimal reaction time on reductio of FFA concentration in soybean oil- olei acid mixture is 150 min in the presence o 1.0% catalyst.

CONCLUSIONS

The study on the optimization of pre-treatment process to reduce FFA concentration in citrus seed oil in the presence of acid catalyst is carried out under various parameters effecting the reaction such as ratio of methanol (%v/v), percentage of catalyst loading (wt%), and reaction time (min). Design expert of response surface methodology (RSM) is employed to determine and evaluate the experimental work model. Twenty runs of experiment are required to optimize the model of pre-treatment process. The optimized conditions are 112 min of reaction time, 48 %v/v of methanol ratio, and 0.92 wt% of catalyst loading. The lowest FFA concentration obtained is < 1.0%.

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