Numerical optimization for esterification of waste coffee grounds oil using reaction external approach

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ABSTRACT
Biodiesel is alternative bio-fuel to substitute for diesel fuel which produces harmful emission causing environmental problems. The common feedstock for biodiesel production was edible oil which effected to high production cost. In order to conquer this problem, waste material was appeared to be an attractive choice. The oil from waste coffee grounds (WCGs) has the potential to use as raw material. However, high free fatty acid (FFA) concentration (>1%) in extracted oil from WCGs requires pre-treatments prior to trans esterification. Therefore, FFA was treated by using sulfuric as acid catalytic. In this study, the optimization of esterification of extracted oil from WCGs was investigated by using response surface methodology (RSM). The effect of operation parameters to pre-treatment of FFA was conducted using laboratory scale. The predicted optimum condition results indicated that %FFA of the waste coffee grounds oil (WCGO) was dec reased 94.97% when the condition was carry out with methanol 10 mole per mole of FFA in the presence of 15% w/w of %FFA-to-catalyst ratios for 115 min reaction time at 65°C.

KEYWORDS: Predictive Analysis, Urban Planning, Innovation Adoption, Machine Learning

1.0 INTRODUCTION

Biodiesel is an alternative, renewable and biodegradable energy produced from biological resources using trans esterification or esterification reactions. Its properties are close to that of petroleum which can be used alone or blended with diesel in unmodified diesel-engine vehicles. Moreover, it also reduces both the amount of fossil fuels burned and the emission of greenhouse gases such as CO2 [1-7]. Currently, the main feedstock for biodiesel production is edible vegetable oils because they get high biodiesel yield due to low FFA content. However, the using of edible oils as the feedstock is a major hurdle to commercialization because it is high cost and 75% of biodiesel production cost is raw material [6-13]. In addition, the biodiesel production from edible oils can lead to food oil crisis [3]. Thus, these factors have the negatively effects on its production from edible oils. Therefore, many non-edible oils, e.g. rubber seed oil, Jatropha oil, she abutter, chicken fat and WCGO have become more attractive as an alternative feedstock because of priceless and easy processing [14-19]. Coffee has a great commercial in Thailand because 75,000 tons of coffee bean were produced in 2014 [19-25]. Considering this huge amount of WCGs, some attempts for reutilization should be made. The WCGs contain 11 to 20 wt% of oil depending on its type [23-27]. Therefore, WCGO is expected to be a new resource for the biodiesel production process. However, non-edible oils usually contain high FFA (>1%) and are too far beyond the level that could be conducted into one step trans esterification. Because FFA could react with the base catalyst which leading to the soap formation [25-32] through the undesirable saponification reaction. Pretreatment by esterification reaction was mentioned in order to remove the FFA content before biodiesel production. In the present study, the esterification of WCGO in the presence of acid catalyst was conducted to reduce the %FFA. The aim of this investigation was to study the effect of methanol to FFA mole ratio, amount of catalyst, reaction temperature and reaction time on the esterification reaction. The central composite design (CCD) of RSM was used to design of experiments for generating the model and optimizing the operational parameters [30-39].

2.0 METHODOLOGY

This study, WCGs were collected from Southern coffee shop (Tesco Lotus, Nakhon Si Thammarat branch) which were a mixture of Arabica and Robusta. AR grade methanol was purchased from Fisher Scientific. Concentric sulfuric acid was from Loba chemie. Hexane was purchased from J.T. Baker. The WCGs were dried in an electrical oven at 105°C for 24 hrs. [1-10] to get rid of its moisture content. Dried WCGs were extracted using hexane as a solvent. The solid-

liquid mixture was stirred for 5 mins. The extracted solvent was separated from the WCGs by filtration. The WCGO was separated from the solvents by using a vacuum rotary evaporation. The WCGO was left in the oven for 6 hrs. at 105°C to remove any hexane that remains in the extracted oil. The fatty acid composition was analyzed by Gas Chromatography-Flame Ionization Detector (GC-FID) according to In-house method of Scientific Equipment Center, Prince of Songkla University [11-20]. The esterification of WCGO was carried out in 250 mL round-bottomed flask connected to reflux condenser, thermometer and hot plate with magnetic stirrer. The WCGO was reacted with methanol in the presence of sulfuric acid. The variables for optimization were selected and given in Table 1. The reaction product mixture was poured into a separating funnel in order to separate the layer of oil and water. The upper layer was washed with hot water to remove acid catalyst and heated to remove water content [1-9].

Table 1. Variables used for optimizing in esterification of WCGO

Variables	Symbols	Low value	High value
Methanol to FFA mole ratio	A	5	15
Catalyst (%wt)	B	5	15
Temperature (^{0}C)	C	50	70
Time (mins)	D	30	120

The FFA was analyzed based on AOCS official method Ca 5a- 40 [7] . Esterified product was accurately weight around 1 – 10 g into 250 mL Erlenmeyer flask [21-29]. Then, 50 mL of alcohol was added and vigorously shaken to dissolve the sample. Phenolphthalein was added of 2 – 3 drops as indicator. The mixture was titrated with 0.1 N NaOH until appearing of a permanent pink color. The FFA content could be calculated according to the following Eq. (1)

$$\%\text{FFA} = \frac{V \times C \times 26.75}{m} \quad (1)$$

where and are volume (mL) and concentration (mol/ L) of NaOH, is mass of the sample (g) and 26. 75 is the average molecular weight of WCGO's fatty acid (%wt). A four-factor CCD of RSM was used to design the experiment for determining the effect of variables on %residue of FFA. The experimental results were analyzed to fit model by the response surface regression. The evaluation of developed model was done for predicting the performance of the response of the esterification process [11-18]. The parameters including Fisher's test (F-value), the probability value (p-value), correlation coefficient (R) and coefficient of determination (R2) were used for this purpose. Also, diagnostic plots, such as normal % probability and student zed residual plot, student zed residuals and predicted response plot and the actual and predicted plot were also used to adequacy of the model. The quadratic equation model for predicting the optimal condition is as follow Eq. (2)

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_i \sum_{<j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where is the response (% residue FFA), and are the independent factors, is the intercept value, and are the coefficients for linear, quadratic and interaction effect, is the error and is the number of factors. WCGO was characterized to analyze its properties to use as a feedstock for biodiesel production. The results shown that the highest fatty acid composition of WCGO was linoleic acid (42%), followed by palmitic acid (33%) and oleic acid (9%). This was similar to exiting work reported in literature [27-39]. Based on its fatty acid, the average molecular weight was 843 g/ mol. The moisture content and % FFA of the WCGO were 0. 236% and 16. 5% , respectively. The characteristic of WCGO showed that WCGO was a good resource for biodiesel production, but %FFA should be first reduced by esterification reaction. The experiment for esterification of WCGO was designed using RSM provided by Minitab software version 17. The 31 experiments were generated by CCD model with 5-level-4-factor to optimize the esterification parameters for aiming at the minimal FFA values [8-16]. All combinations consist of 16 factorial points, 8 axial points and 7 replicates at the center point to check the error and reproducible of the data [13-28]. The experimental designs with actual level of process factor were presented in Table 2. Experimental

results of esterification of WCGO with acid catalyst were presented in Table 2. The least squares regression was used to fit the data for generating equation and it was evaluated the statistical significance of the parameters by ANOVA. The best fit model in term of the actual values was described by Eq. (3)

$$\%\ \text{Residue FFA} = 77.60 - 0.356A - 2.585B - 1.984C + 0.1650D + 0.03063A^2 + 0.05763B^2 + 0.01971C^2 + 0.000529D^2 + 0.06320AB - 0.02900AC + 0.009956AD + 0.01600BC - 0.004089BD - 0.005533CD \quad (3)$$

The results of mathematical model analysis were summarized in Table 3. At 95% confidence level (p- value <0. 05), the model shown that F- value and p- value were 92. 45 and <0. 001, respectively, which indicated that model term are significant. The significance of each parameter of Eq. 3 (both individual and interacting parameters) could be seen from p- value also. The p- value of linear, square and two- way interaction were <0. 001, suggesting that all parameters influenced to FFA reduction. The smaller the p-value, the more significant is the corresponding coefficient [27-39]. The goodness of fit of the developed model could be described by R2. The calculated values of R2, adjusted R2 and predicted R2 were 0. 9878, 0. 9771 and 0. 9306, respectively. High value of R2 which is reasonably close to 1, shown that there was a good correlation between results of experimental values and prediction values by the model equation.

Table 2. Experimental design and results on esterification of WCGO

Run	Variables				% Residue FFA	Run	Variables				% Residue FFA
	A	B	C	D			A	B	C	D	
1	10.0	10.0	60	75.0	2.37	17	12.5	7.5	65	97.5	1.73
2	7.5	7.5	55	97.5	4.83	18	7.5	12.5	55	52.5	4.01
3	12.5	12.5	65	52.5	3.54	19	12.5	12.5	55	97.5	4.57
4	7.5	7.5	65	52.5	5.77	20	10.0	10.0	60	75.0	2.30
5	7.5	12.5	65	52.5	4.85	21	10.0	10.0	60	75.0	2.28
6	7.5	12.5	55	97.5	2.78	22	15.0	10.0	60	75.0	2.68
7	10.0	15.0	60	75.0	3.08	23	12.5	7.5	65	52.5	2.09
8	10.0	10.0	70	75.0	2.40	24	12.5	7.5	55	97.5	5.43
9	12.5	7.5	55	52.5	3.97	25	10.0	10.0	60	30.0	4.85
10	5.0	10.0	60	75.0	3.40	26	10.0	5.0	60	75.0	4.35
11	10.0	10.0	50	75.0	6.09	27	7.5	12.5	65	97.5	0.86
12	12.5	12.5	55	52.5	3.80	28	10.0	10.0	60	75.0	2.27
13	10.0	10.0	60	75.0	2.23	29	7.5	7.5	65	97.5	2.53
14	12.5	12.5	65	97.5	1.34	30	10.0	10.0	60	75.0	2.26
15	7.5	7.5	55	52.5	5.66	31	10.0	10.0	60	120.0	1.84
16	10.0	10.0	60	75.0	2.32						

The residual plots were examined for the model adequacy checking in Fig. 1a – 1d. The outlier t plot for all experiments of esterification reaction was shown in Fig 1a. It shown values between ±3. 0 which indicated that the approximation of the fitted model to the response was fairly good with no data recording error [13-29]. The normal % probability and studentized residual plot was used to show the distribution pattern of the data. As shown in Fig 1b, the residuals quite closed to a straight line indicating that they were normally distributed in the model response. The relationship between studentized residuals and predicted response (Fig 1c) shown that the points lain below the interval ±3. 5. This indicated that there was no need for transformation of the response variable. The predicted values versus actual values were shown in Fig 1d. The data have linear behavior and are distributed close to diagonal line. Therefore, the obtained second-order polynomial model is quite satisfactory for predictions of %FFA residue from esterification reaction [23-39].

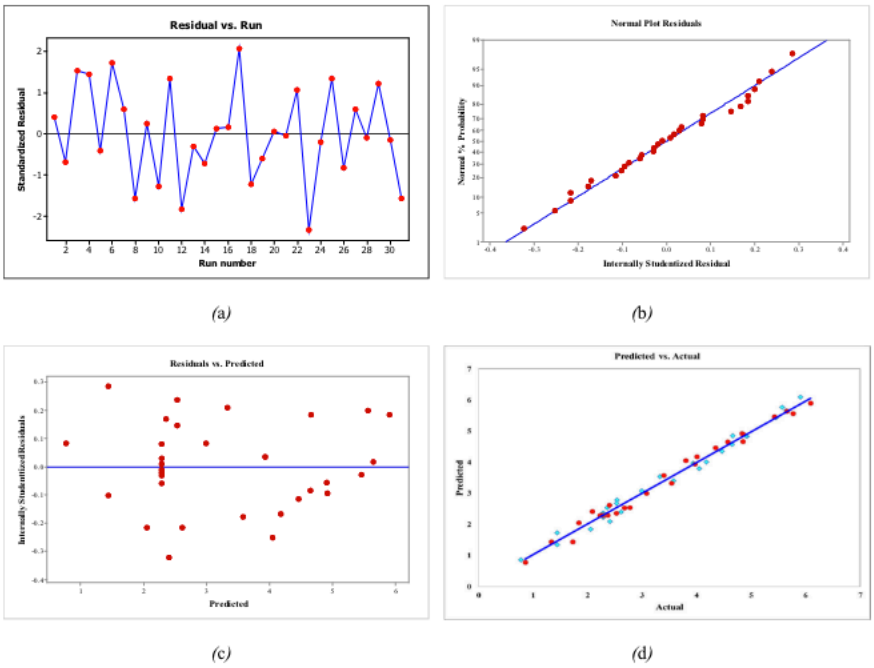

Fig. 1. (a) The outlier t plot (b) normal % probability and studentized residual plot
(c) studentized residuals and predicted values plot (d) actual values and predicted values plot

he optimization of response was performed to reduce the %FFA (<1%) based on developed mathematical model. Since the obtained model (Eq. 3) offered satisfy estimation to the experimental conditions, it was employed to predict the optimum conditions for receiving the designed %FFA content. The % FFA was 0. 83 when the methanol to FFA ratio was 10, amount of catalyst was 15wt%, reaction time was 115 mins and reaction temperature was 65°C.

Table 3. Analysis of variance (ANOVA) of the response surface quadratic model

Source	df	Sum of squares	Mean square	F value	p-value*
Model	14	59.5018	4.2501	92.45	<0.001
Linear	4	31.2548	7.8137	169.97	<0.001
Square	4	10.9440	2.7360	59.52	<0.001
Two-way interaction	6	17.3030	2.8838	62.73	<0.001
Residual	16	0.7355	0.0460		
Pure error	6	0.0124	0.0021		
Cor total	30	60.2374			
$R^2 = 0.9878$	R^2 (adj) = 0.9771	R^2 (pred) = 0.9306			

* p-value < 0.05 statistically significant at the confidence level of 95%

4.0 CONCLUSION

The removal of %FFA in WGCO by esterification using CCD based on RSM was studied. Optimizing four operating parameters, methanol to FFA mole ratio, amount of catalyst, reaction temperature and reaction time, led to a minimum %FFA (<1%) via esterification reaction. The proposed mathematical model was successfully used to predict the effect of parameters to reduce the FFA content. The suitability of received model was proved with high adjusted correlation coefficients. It was concluded that the predicted values by statistical model were close to experimental values. Under optimum condition predicted by model, the FFA of WCGO was reduced 94.97%

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