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OPTIMIZATION OF METHYL ESTER PRODUCTION FROM PALM FATTY ACID DISTILLATE USING SINGLE-STEP ESTERIFICATION: A RESPONSE SURFACE METHODOLOGY APPROACH

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ABSTRACT

In this study, the optimization of three parameters: methanol (33–117.1 wt.%), sulfuric acid (1.6–18.4 wt.%), and reaction time (12.7–147.3 min) for methyl ester production from palm fatty acid distillate (PFAD) were investigated by using the response surface methodology (RSM). The single-step esterification was carried out to determine the highest percentage of methyl ester production from PFAD using a batch reactor with a six-blade turbine impeller at fixed 300 rpm. The results showed that the 97.028 wt.% actual experimental conversion of ester were obtained, when the optimal condition: 100.6 wt.% methanol, 9.4 wt.% sulfuric acid, and 91.5 min reaction time was carried out at 60 ^{o}C. Moreover, the 115.97% crude biodiesel yield and 99.63% biodiesel yield were achieved, after through the separation and purification processes.

Keywords: palm fatty acid distillate, esterification, optimization, response surface methodology.

INTRODUCTION

The palm fatty acid distillate (PFAD) was commonly used in the animal feed industry, soap industry, and oleochemical industry (Tay *et al.,* 2009), (Tapanwong and Punsuvon, 2011), (Gapor Md Top, 2010). The vitamin E in PFAD can be extracted to produce for cosmetics and pharmaceutical industries (Ahmadi *et al.*, 2012). Thailand is the world's third largest producer of crude palm oil (USDA, 2015). Moreover, the approximately 2 million tonnes of crude palm oil (CPO) production can be produced in 2014 (USDA, 2015). In addition there is no the official production data of PFAD, however, the estimated PFAD production is based on the approximately 4% of FFA in CPO (Gapor Md Top, 2010), as shown in Table I. The PFAD is the light yellow solid at 30 ^{o}C of room temperature and the major composition is the free fatty acid (FFA), which consists of palmitic acid, oleic acid, and a small percentage of tri-, di-, and mono-glycerides (Chongkhong e*t al.*, 2007). Therefore, an acid-catalyzed direct esterification was adopted to directly convert the high FFA in PFAD to ester, as expressed in equation (1) (Somnuk *et al.*, 2013). Moreover, the ester conversion was not decreased by the formation of soap, thus, the high yield of ester will obtained by esterification. (Deshmane *et al.*, 2009), (Rahmi and Neswati, 2013).

Currently, few researchers have studied the use of the single-step esterification with acid catalyst for the biodiesel production from PFAD. Chongkhong *et al.* (2007) studied the overflow system for continuous esterification of PFAD using the continuous stirred tank reactor (CSTR). The FFA in PFAD can be reduced from 93 to 1.5 wt.%, when the optimal condition: 8.8:1:0.05 molar ratio of methanol to PFAD to sulfuric acid, 60 min of residence time at 75 ^{o}C, was conducted. The properties of methyl ester meet the specification of American standard. Tapanwong and Punsuvon (2011) studied the optimization of ester production from PFAD with oleyl alcohol in the presence of Amberlyst 15. The results showed that the 81.52% ester and 80.54% yield of biodiesel were achieved under the optimal condition: 33 wt.% acid catalyst, 95 min of reaction time, and 1:2.7 molar ratio of fatty acid to oleyl alcohol. Rahmi and Neswati (2013) studied the biodiesel production from PFAD by using a refluxed batch reactor. The FFA in PFAD was reduced from 97.17 wt.% to less than 10 wt.%, when the single-step esterification of PFAD were carried out under the condition: 10:1 molar ratio of methanol to PFAD, 2 wt.% sulfuric acid, and 60 ^{o}C reaction temperature at 60 min reaction time. The above reviews induce the objective of this study was to optimize the highest percentage of methyl ester production from PFAD with single-step esterification, when the three independent variables: methanol, sulfuric acid, and reaction time were investigated by using the RSM.

$$\text{FFA} + \text{Alcohol} \xleftrightarrow{\text{acid - catalyst}} \text{Ester} + \text{Water} \qquad (1)$$

Table-1. Total production of CPO and estimated PFAD production in Thailand (Unit: Tonne).

Year	CPO production [USDA, 2015]	Estimated PFAD production
2009	1,287,000	51,480
2010	1,832,000	73,280
2011	1,892,000	75,680
2012	2,135,000	85,400
2013	2,150,000	86,000
2014	2,250,000	90,000

MATERIALS AND METHODS

Materials

The palm fatty acid distillate (PFAD) is the by-product from the refining process of refined palm oil (RPO) to eliminate the free fatty acid (FFA) in the crude palm oil (CPO) by the deacidification and deodorization

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process (Gapor Md Top, 2010), (Cho *et al.*, 2013). The PFAD was purchased from a large-commercial-scale palm oil extracting and refining facilities in eastern Thailand. The PFAD containing 90.417 wt.% of FFA with a mean 265.5 g/mol molecular weight, 0.861 kg/L (at 60 °C) of density, was used as the raw material for the single-step esterification reaction, as shown in figures 1(a) and 1(b) at 30 °C of room temperature, and 43 °C of melting temperature, respectively.

Analysis

All chemicals include the 98% methanol, 99% sulfuric acid, are the commercial grade. A thin layer chromatograph with flame ionization detection (TLC/FID) was used to analyze the purity of methyl ester (ME), triglyceride (TG), diglyceride (DG), monoglyceride (MG), and FFA in the biodiesel from PFAD. The physical properties and compositions of PFAD and biodiesel are shown in Table II. Figure 1(c) shows the products after complete esterification reaction under the optimal condition. The products were slowly poured into the glass bottle and allowed to completely separate into the two layers. The top layer is the methyl ester, and the bottom layer is the wastes, which consist of the main component is the water, and some of methanol, and sulfuric acid. The yield of biodiesel production from PFAD was determined by using following equation (2).

$$Y = (W_{biodiesel} \;/\; W_{PFAD}) \times 100 \qquad (2)$$

where Y is the yield of biodiesel, W_{PFAD} (g) is weight of PFAD, and $W_{biodiesel}$ (g) is the weight of biodiesel.

Figure-1. Palm fatty acid distillate (a) 30 °C room temperature, (b) 43 °C melting temperature, and (c) products after complete esterification reaction (top layer: crude biodiesel, and bottom layer: waste).

Table-2. Physical properties and compositions of PFAD and biodiesel under optimal condition.

Property	PFAD	Biodiesel
Mean molecular weight (g/mol)	265.5	-
Density (kg/L)	0.861(60°C)	0.875(15°C)
Free fatty acid (wt.%)	90.417	0.736
Tri-glyceride (wt.%)	1.200	0.000
Di-glyceride (wt.%)	2.437	1.849
Mono-glyceride (wt.%)	5.041	0.387
Ester (wt.%)	0.874	97.028
Acid value (mgKOH/g)	265	2.537

Methods

Figure-2 is a schematic diagram of the experimental apparatus of the single-step esterification for the batch process. The circulating hot water bath was used to control the reaction temperature in the 2000 mL of wide neck reaction flasks by circulating pump. An initial procedure for batch process, the fixed 600 g of PFAD was scooped into the flasks. Subsequently, the PFAD was heated and stirred to melt by heater and impeller, respectively. The required methanol was added into the flask. The reaction was started when the sulfuric acid was unhurriedly dropped by the burette. Since, the reaction temperature of the mixture will increase when the loading sulfuric acid was added too early, until the temperature of mixture exceeded the boiling point of methanol (64.7 °C). Therefore, the temperature of mixture will be carefully observed by the digital temperature with thermocouple in the flask, while the sulfuric acid was dropped by burette. The temperature of mixture was maintained at 60 °C for desired time, and was vigorously mixed by the six-blade turbine impeller at fixed 300 rpm. The effects of two reactants: methanol (33–117.1 wt.%), and sulfuric acid (1.6–18.4 wt.%) were investigated, and optimized the highest purity of ester, as shown in the experimental design matrix (Table III). For the sampling time, all samples were collected at the desired reaction time (12.7–147.3 min). Each sample was rapidly cooled with 0 °C water to stop esterification reaction (Intarat *et al.*, 2014). Subsequently, the samples were then washed with the hot water to eliminate the residual acid-catalyst and methanol in the samples, until the potential of hydrogen ion (pH) of wash water is equal to 7. The thin layer chromatography/flame ionization detection technique (TLC/FID) were analyzed to analyze the purity of methyl ester in the samples.

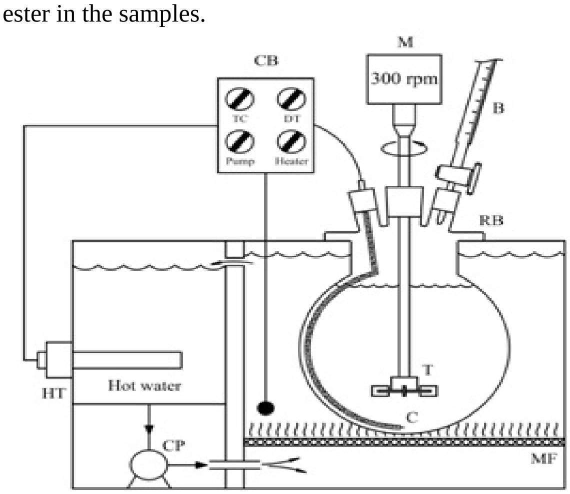

Figure-2. Schematic diagram of the experimental setup. (HT: heater, CB: control box, CP: circulating pump, M: motor, TC: temperature control, DT: digital temperature, B: burette, RB: round bottom flask, T: six-blade turbine impeller, C: thermocouple, and MF: mesh filter).

Table-3. Coded level of independent variables.

Variable		Coded level				
		-1.682	-1	0	+1	+1.682
M	: Methanol (wt.%)	33	50	75	100	117.1
S	: Sulfuric acid (wt.%)	1.6	5	10	15	18.4
T	: Reaction time (min)	12.7	40	80	120	147.3

Experimental Design

In the optimization of analytical methods, the response surface methodology (RSM), with 5-level and 3-factor of central composite design (CCD), was used to determine the optimal condition for the methyl ester production from PFAD by using the single-step esterification. The regression analysis was adopted to fit a second-order polynomial equation of methyl ester in the product. A form of general second-order polynomial equation is expressed in equation (3) (Tapanwong and Punsuvon, 2011). The methanol (*M*), the sulfuric acid (*S*), and reaction time (*T*) are the three independent variables, which were studied in the biodiesel production from PFAD for converting the major FFA to methyl ester (*E*).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where *Y* is the response (methyl ester, wt.%); x_i and x_j are the uncoded independent variables (methanol, sulfuric acid, and reaction time); β_0, β_i, β_{ii}, and β_{ij} are the intercept, linear, quadratic and interaction constant coefficients, respectively; k is the number of variables, and ε is the error.

RESULTS AND DISCUSSION

Experimental Results

Experimental results and response surface model of single-step esterification with acid catalyst were presented in Table IV. As stated in the procedure section, the eighteen-test were conducted to analyze the ester content in each condition for the methyl ester production from the PFAD. It was found that when these mixtures were taken to analyze the ester, the purity of methyl ester are in the range between 86.781 and 96.499 wt.% by TLC/FID.

Response Surface Model and Statistical Analysis

The RSM of acid-catalyzed esterification was analyzed with the experimental design and the results from Table IV, by using a multiple regression model to fit a second-order polynomial equation (Intarat *et al.*, 2014). The predicted model of relationship between the methyl ester and the three independent variables were obtained in the form of a full quadratic model, as expressed in equation 4. The statistical analysis value of this model is defined by the coefficient of determination (R^2), standard error, the adjusted coefficient of determination ($R^2_{adjusted}$), and *p*-value, as shown in Table V. As a result, the methanol concentration shows to be the most significant term of $\beta_1 M$ in the quadratic model, because, the *p*–value of this constant coefficient is the lowest value when compared with the other terms. Consequently, the volume of methanol is the highest significant parameter for converting the FFA of PFAD to ester by the single-step direct esterification for batch process.

$$E = \beta_0 + \beta_1 M + \beta_2 S + \beta_3 T + \beta_4 M^2 + \beta_5 MS + \beta_6 MT + \beta_7 S^2 + \beta_8 T^2 \quad (4)$$

where *E*: ester, *M*: methanol, *S*: sulfuric acid, *T*: reaction time, and β: coefficient value.

Response Surface Plots

Figures 3, 4 and 5 show the relationship between the methyl ester and independent variables, which are presented using the response surface plots. The effects of sulfuric acid and methanol (Figure 3), reaction time and methanol (Figure 4), and reaction time and sulfuric acid (Figure 5), on the purity of methyl ester production from PFAD.

Optimum Conditions of Methyl Ester Production

The optimal condition for the single-step esterification was used to produce the methyl ester from PFAD, which is analyzed by TLC/FID method, are shown in figures 3, 4, and 5. The solver function in Microsoft Excel was used to determine the optimal condition for methyl ester production from PFAD. The 96.709 wt.% of highest purity of ester was obtained when the optimal condition for predicted model: 100.6 wt.% methanol, 9.4 wt.% sulfuric acid, and 91.5 min reaction time was carried out under the atmospheric pressure at 60 °C reaction temperature. To verify the predicted model (equation (4)), the optimal condition of model was adopted for proving the purity of methyl ester by the experiment. The results showed that the 97.028 wt.% actual experimental conversion of ester was achieved which close to the percentage of ester from predicted model. Therefore, this equation has the high confident level for predicting the percentage of ester from the single-step esterification process from PFAD. Moreover, the 115.97% crude biodiesel yield and 99.63% biodiesel yield were achieved with optimal condition, after each product through the separation and purification processes.

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Table-4. Experimental design matrix.

Run	Methanol, *M* (wt.%)	Sulfuric acid, *S* (wt.%)	Reaction time, *T* (min)	Ester, *E* (wt.%)
1	50.0	5	120	93.404
2	33.0	10	80	88.827
3	50.0	15	40	90.919
4	75.0	10	80	95.608
5	50.0	5	40	86.781
6	117.1	10	80	96.333
7	100.0	15	40	95.056
8	75.0	10	80	95.134
9	100.0	5	40	95.093
10	100.0	5	120	96.499
11	75.0	10	80	95.708
12	75.0	10	80	95.470
13	100.0	15	120	95.953
14	50.0	15	120	95.352
15	75.0	1.6	80	92.502
16	75.0	10	12.7	91.208
17	75.0	10	147.3	95.437
18	75.0	18.4	80	95.370

Table-5. Coefficient values of response surface model.

Coefficient	Value	*p*-value	Std Error	-95%	95%
β_0	60.39	0.000000002	2.550	54.62	66.15
β_1	0.459	0.00000348	0.04579	0.356	0.563
β_2	1.004	0.000365	0.182	0.594	1.415
β_3	0.185	0.0000187	0.02269	0.134	0.237
β_4	-0.00147	0.000310	0.000260	-0.00206	-0.000884
β_5	-0.00667	0.00277	0.00164	-0.01037	-0.00297
β_6	-0.00109	0.000461	0.000204	-0.00156	-0.000632
β_7	-0.01763	0.02394	0.00650	-0.03234	-0.00292
β_8	-0.000411	0.00291	0.000102	-0.000641	-0.000181

(R^2 = 0.977, $R^2_{adjusted}$ = 0.957, and R^2 for prediction = 0.882)

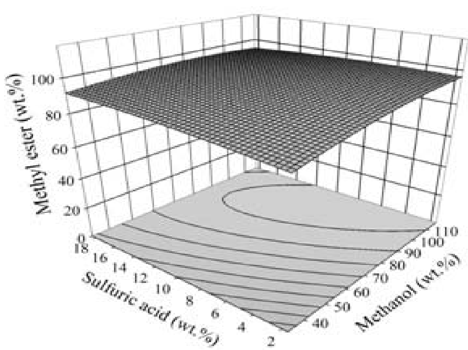

Figure-3. Surface plot of sulfuric acid and methanol on the purity of methyl ester.

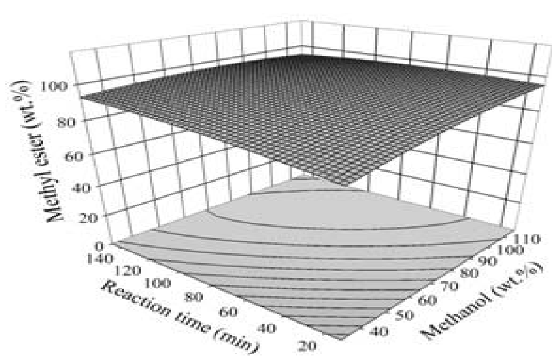

Figure-4. Surface plot of reaction time and methanol on the purity of methyl ester.

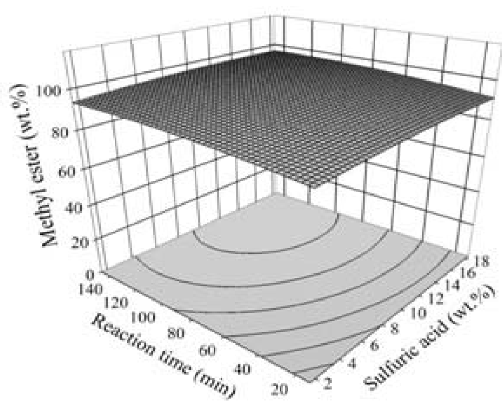

Figure-5. Surface plot of reaction time and sulfuric acid on the purity of methyl ester.

CONCLUSIONS

The single-step esterification process of methyl ester from palm fatty acid distillate (PFAD) with MeOH in the presence of the H_2SO_4 as the strong acid catalyst was employed to directly convert the high FFA in PFAD to ester. The 96.709 wt.% of highest purity of ester was obtained from the predicted model, when the optimum condition: 100.6 wt.% methanol, 9.4 wt.% sulfuric acid, 91.5 min reaction time, 60 ºC reaction temperature was used. The model was verified to proof the predicted purity of ester. It was found that the 97.028 wt.% of ester was achieved, which close to the percentage of predicted ester.

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Moreover, the 99.63% yield of biodiesel from PFAD was succeeded under the optimal condition.

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