Optimization for Community Biodiesel Production from Waste Palm Oil via Two-Step Catalyzed Process

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Abstract: The objective of this research was to develop technique to prepare biodiesel from WPO (Waste palm oil) with high free fatty acid contents using a two-step. The process consists of esterification and transesterification steps. RSM (Response surface methodology) was applied for investigating the experimental design for esterification step. These were 20 experiments involving the three investigated variables of methanol to FFA (Free fatty acid) of WPO ratio, amount of sulfuric acid catalyst and reaction time that were studied on esterification to optimize the condition for decreasing FFA in WPO to less than 2% wt.. The WPO with low FFA was further experimented in transesterification step to obtain fatty acid methyl ester. The investigated results showed that the WPO containing 48.62% wt. of high FFA and the optimum condition of esterification step was 28 mol of methanol to FFA in WPO molar ratio, 5.5% sulfuric acid concentration in 90 min of reaction time and 60 °C of reaction temperature. Waste palm oil biodiesel with optimized condition in two-step catalyzed process gave methyl ester content at 84.05% according to EN (European standard) 14103 method. The properties of waste palm oil methyl ester met the standards of Thai community biodiesel.

Key words: Biodiesel, waste palm oil, free fatty acid, esterification.

1. Introduction

Biodiesel is the mono alkyl esters of long chain fatty acids. It is a chemically modified fuel derived from various kinds of vegetable oils and animal fats which are composed primarily of high molecular weight triglycerides [1, 2]. It is renewable clean bio-energy and has no sulfur content. The quality of biodiesel is similar to diesel fuel, thus it becomes a promising alternative to diesel fuel [3]. Biodiesel can be made from renewable source such as edible oils, but the value of edible oils is high, so the cost in biodiesel production is high. Therefore, exploring ways to reduce the cost of raw material are the main interest in recent biodiesel research.

Waste palm oil in the wastewater pond is one factors of low cost raw material for making biodiesel. This waste palm oil or crude palm oil leaks about 1-2% from the milling process of the fresh fruit bunches and drains

into wastewater pond. In Thailand, it finds that the amount of leaked waste palm oil in the wastewater pond is more than 2,000,000 tons/year. The current applications of waste palm oil are to use in the low-grade soap production and boiler fuels. The use of waste palm oil can reduce the cost of biodiesel production which makes them of high potential alternative feed stock. The waste palm oil usually contains high amount of FFA (Free fatty acid) that is not converted to biodiesel product by one step (the alkaline catalyzed process), it causes to produce soap that prevent the separation of biodiesel from glycerin fraction [4, 5]. So, the two-step catalyzed processes are suitable for biodiesel production from waste palm oil. The first step is esterification step that uses acid catalyze to reduce FFA in the waste palm oils to less than 2%. The second step is transesterification step that uses alkaline catalyze to change the triglycerides that remain in waste palm oil to mono-ester or biodiesel.

RSM (Response surface methodology) is a useful statistical technique which has been applied in research

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into complex variable process. The multiple regression and correlation analyses are used as tools to assess the effect of two or three independent factors on the dependent variables. In addition, the CCD (Central composite design) of response surface methodology has been applied in the optimization of several biotechnological and chemical processes. The principle advantage of RSM is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable result. RSM has been successfully applied in the study and optimization of biodiesel production in fat and oil feed stock [6, 7].

In this work, the biodiesel was produced from waste palm oil via two-step catalyzed process. The esterification step is studied to optimize condition by RSM. The FFA in WPO (Waste palm oil) was reduced to less than 2% wt. in the first step. Then the FAME (Fatty acid methyl ester) was produced in the transesterification step. After that FAME was analyzed for properties of biodiesel quality by ASTM (American society for testing and materials) and EN (European standard) standard methods.

2. Materials and Methods

2.1 Materials

WPO was collected from a wastewater treatment pond of the palm oil mill plant in Thailand. The chemicals for this research were methanol, sulfuric acid, sodium hydroxide, potassium hydroxide, sodium chloride, N- heptanes (C_7H_{16}), methyl heptadecanoate, etc. They are analytical grade. The reference standards of FAME were more than 99% purity. (FAME Mix, C8-C24; Supelco Analytical USA).

2.2 Preparation for Material

The solid particles contained in WPO were separated by mixing the WPO with methanol 1:2 by volume at 60 °C for 5 min, after that the mixture product was filtrated on filter paper under vacuum filtration immediately to separate the solid particles from the mixture product. The methanol solution in filtrate was evaporated by

using the rotary evaporator. The water in filtrate was removed by heating operated at 500 rpm at 105 °C for 4 h. The final product was investigated to find the fatty acid composition of WPO by using GC (Gas chromatography) and it was used as the feed stock for making biodiesel in the esterification step.

2.3 Apparatus and Reaction Procedures

Esterification step: The reactions were conducted in 50 ml three-necked flask equipped with a reflux condenser and a thermometer. The flask was heated and stirred with magnetic stirrer on agitator heater, fixed stirred at 700 rpm and temperature reaction at 60 °C. For esterification experiment, the flask was charged with 10 g of WPO and heated to the setting temperature with agitation. A certain quantity of sulfuric acid catalyst was dissolved in the required amount of methanol. After achieving the setting temperature of the reactant and catalyst, methanol and catalyst were added to the flask. The reaction was timed immediately. When the reaction completed to separate the oil from excess methanol, acid catalyst and water, the oil was washed with water and heated at 105 °C. This final product was the feed stock for transesterification step.

Transesterification step: esterified oil (the WPO with less than 2% wt. of FFA contents) obtained from esterification step was further reacted with methanol and potassium hydroxide (KOH) that was used as catalyst. The operation condition was 700 rpm of stirring rate and 60 °C of temperature reaction. When the reaction completed, methyl ester was separated from glycerol. The methyl ester layer was washed with warm 1% NaCl and warm water. After washing, the methyl ester was subjected to heat at 105 °C for removing excess water. Methyl ester was further characterized for physical and chemical properties followed ASTM and EN methods.

2.4 Experimental Design for Esterification Step

A five-level and three-factor CCD with 20

experiments were employed in this study. Methanol to FFA in waste palm oil molar ratio (M), acid catalyst concentration (C) and reaction time (T) were the independent variables to optimize the reduction of FFA in WPO. The coded and uncoded levels of the independent variables, independent factor, levels and experimental design were shown in Table 1. The central values (zero level) chosen for experimental design were 20:1 (wt./wt.) of methanol to FFA in waste palm oil molar ratio, 5.00% (wt./wt.) of acid catalyst concentration and 120 min of reaction time.

2.5 Statistical Analysis

The experimental data of the esterification step was performed by the RSM that followed a second-order polynomial equation generated SPSS (Statistical package for social science) software. The suitable model was used to generate a response surface plot by STATISTICA software. The quadratic response surface model was shown in Eq. (1):

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 \beta_{ij} X_i X_j \quad (1)$$

where, Y is the response (FFA; % wt.), β_0 is constant, X_i and X_j are the independent variables, β_i and β_j are the linear term coefficients, β_{ii} is quadratic term coefficients, and β_{ij} is the interaction constant coefficients. SPSS package was used for regression ANOVA (Analysis of variance) and response surfaces methodology was performed using the SPSS software [8].

2.6 Analytical Methods

2.6.1. Free Fatty Acid Content Analysis

The FFA was determined via AOCS official method Ca5a-40 standard method. 7 g of sample was

introduced into a 250 ml flask, after which 75 ml of pre-neutralized 95% ethanol solution and 2 ml of 1% phenolphthalein solution (1 g of phenolphthalein in 100 ml of ethanol) were added into the flask and titration with 0.1 N sodium hydroxide solution. The FFA content was calculated in accordance with the following Eq. (2):

$$\text{Free Fatty Acid} = \frac{(A - B) \times N \times 25.6}{W} \quad (2)$$

where, A is milliliter of sodium hydroxide solution titrated with sample, B is milliliter of sodium hydroxide solution titrated with blank, N is the concentration of sodium hydroxide in normality unit, and W is the weight in gram of sample.

2.6.2. Fatty Acid Methyl Esters Content

The content of FAME were measured via standard EN 14103. The analyses were conducted on a gas chromatography (agilent technologies GC-6890) using a fused silica capillary column (DB-WAX, agilent technologies, USA) and a flame-ionization detector with an injection temperature of 270 °C, and a detector temperature of 270 °C. The spit ratio was 30:1. The FAME content was calculated via the following Eq. (3):

$$\text{Methyl ester} = \frac{\sum A - A_{is}}{A_{is}} \times \frac{C_{is} \times V_{is}}{W} \times 100 \quad (3)$$

where, methyl ester content has unit in % wt., $\sum A$ is the total peak area of methyl ester, A_{is} is the peak of methyl heptadecanoate which use as internal standard, C_{is} is the concentration of methyl heptadecanoate solution (mg/mL) V_{is} is the volume of methyl heptadecanoate solution (mL), and W is the weight in milligram of sample.

Table 1 Independent variables and levels used for CCD for esterification step.

Variables	Symbols (Uncoded)	Code levels ^a				
		- 1.68 (- α)	- 1	0	+ 1	+ 1.68 (+ α)
Methanol to FFA in waste palm oil molar ratio	M	11.6:1	15.0:1	20.0:1	25.0:1	28.4:1
H ₂ SO ₄ concentration (% wt./wt.)	C	3.32	4.00	5.00	6.00	6.68
Reaction time (min)	T	69.6	90	120	150	170.4

^a Transformation of variable levels from code (X) to uncoded could be obtained as: $M = 20 + 5X$, $C = 5 + 1X$ and $T = 120 + 30X$.

2.7 Characterization of Waste Palm Oil Methyl Ester Properties

The WPO methyl esters were characterized by determining its viscosity, density, flash point, acid value, water and sediment and methyl ester. The following test methods were used: density at 15 °C (ASTM D 1293), Viscosity at 40 °C (ASTM D 445), flash point (ASTM D 93), acid value (ASTM D 664), water and sediment (ASTM D 2709) and methyl ester content (EN 14103).

3. Results and Discussion

3.1 Properties of Waste Palm Oil

The investigation results of the properties of waste palm oil indicated that the physical and chemical properties of the waste palm oil, the WPO had the water content of 0.28% and the FFA contents of 48.62% which is needed to reduce to less than 2% by using the esterification process. The fatty acid compositions of waste palm oil determined by GC were shown in Table 2. They are very important to identify the carbon chains and their properties. Palmitic acid (C 16:0) was the major of fatty acid composition in raw material. Saturated and unsaturated fatty acids were 55.62% and 44.37% respectively. The average molecular weight (g/mol) of WPO was determined by a weight average method utilizing the fatty acid profiles. The average molecular weight of fatty acid and waste palm oil were 271 g/mol and 851 g/mol respectively. This average molecular weight was used to calculate the mole ratio of methanol to WPO in transesterification step.

3.2 Optimization of Esterification Step

The design points of the FFA contents used CCD arrangement and response for esterification step were shown in Table 3. The high correlation coefficient (R^2) determined from the regression model of esterification step was shown at Fig. 1. In Tables 4 and 5, statistical

analysis of the model was performed to determine the variance (ANOVA) for the quadratic polynomial model and linear regression coefficients indicated that were obtained by employing a least square technique to predict quadratic polynomial model for FFA.

The characteristics of the models and the coefficients indicated that the predictability of the model was at 95% confidence level. The model had high correlation coefficient, a significant F-value, an insignificant lack-of-fit F-value. The analysis of variance (ANOVA) showed that the model F-values of 13.166 with significance was 0.000 which less than 0.05 for the models, implied the model was significant. The high correlation coefficient ($R^2 = 0.922$) indicated that the model was suitable to represent the real relationships among the parameters studied. The insignificant lack-of-fit which is relative to the pure error of the experiments also indicates that the models were suitable to represent the experimental data. Coefficients of full model equation were evaluated by regression analysis and tested for their significances. The models to predict the FFA content of esterification step was presented in Eq. 4.

$$Y = 30.171 + 0.143 M - 10.384 C + 0.002 T - 0.002 M^2 + 0.958 C^2 + 0.00001513 T^2 - 0.023 MC + 0.001 CT + 0.000 MT \quad (4)$$

3.3 Response Surface Plots of Esterification Step

The optimized levels of variables were determined by constructing three-dimensional surface plots according to Eq. (4). Fig. 2a shows the effect of methanol to FFA in waste palm oil molar ratio (M), acid catalyst amount (C) on the FFA of WPO and their mutual interaction on the FFA of WPO in Fig. 2b

Table 2 Fatty acid compositions of waste palm oil.

Fatty acid	Formula	Structure	wt. %
Myristic	C ₁₄ H ₂₈ O ₂	14:0	0.87
Palmitic	C ₁₆ H ₃₂ O ₂	16:0	47.40
Palmitoleic	C ₁₆ H ₃₀ O ₂	16:1	1.12
Steric	C ₁₈ H ₃₆ O ₂	18:0	4.29

Oleic	C ₁₈ H ₃₄ O ₂	18:1	36.30
Linoleic	C ₁₈ H ₃₂ O ₂	18:2	6.95
Erucic	C ₂₀ H ₄₀ O ₂	20:0	3.06

Table 3 CCD arrangement and response for esterification step.

Treatment	M	C	T	M (mole)	C (%wt./wt.)	T (min)	FFA (%)	
							Experimental	Predicted
1	- 1	- 1	- 1	15.00	4.00	90.00	4.51	4.94
2	- 1	- 1	1	15.00	4.00	150.00	4.53	5.52
3	- 1	1	-	25.00	4.00	90.00	4.35	4.65
4	- 1	1	1	25.00	4.00	150.00	3.79	5.23
5	1	- 1	- 1	15.00	6.00	90.00	2.56	2.82
6	1	- 1	1	15.00	6.00	150.00	2.42	3.52
7	1	1	- 1	25.00	6.00	90.00	1.60	2.07
8	1	1	1	25.00	6.00	150.00	1.55	2.77
9	- 1.68	0	0	20.00	3.32	120.00	6.76	7.64
10	+ 1.68	0	0	20.00	6.68	120.00	3.27	3.80
11	0	- 1.68	0	11.60	5.00	120.00	3.45	3.31
12	0	+ 1.68	0	28.40	5.00	120.00	0.88	2.44
13	0	0	- 1.68	20.00	5.00	69.60	1.57	2.52
14	0	0	+ 1.68	20.00	5.00	170.40	3.13	3.59
15	0	0	0	20.00	5.00	120.00	2.82	3.02
16	0	0	0	20.00	5.00	120.00	2.18	3.02
17	0	0	0	20.00	5.00	120.00	2.82	3.02
18	0	0	0	20.00	5.00	120.00	2.13	3.02
19	0	0	0	20.00	5.00	120.00	1.57	3.02
20	0	0	0	20.00	5.00	120.00	2.10	3.02

Table 4 ANOVA for the quadratic polynomial model of esterification step.

Model	Sum of squares	df	Mean square	F	Sig.
Regression	33.912	9	3.768	13.166	0.000 ^a
Residual	2.862	10	0.286		
Total	36.774	19			

^a Predictors: (Constant), MT, CC, TT, MM, MC, CT, M, T, C.**Table 5** Regression coefficients of predicted quadratic polynomial model for the regression equation of esterification step.

Model	Nonstandardized coefficients		Standardized coefficients	t	Sig.
	B	Std. error	Beta		
1 (Constant)	30.171	7.997		3.773	0.004
M	0.143	0.332	0.436	0.431	0.676
C	- 10.384	1.777	- 6.325	- 5.843	0.000
T	0.002	0.055	0.035	0.034	0.973
MM	- 0.002	0.006	- 0.254	- 0.367	0.722
CC	0.958	0.141	5.867	6.787	0.000
TT	1.513 E-5	0.000	0.067	0.096	0.925
MC	- 0.023	0.038	- 0.453	- 0.609	0.556
CT	0.001	0.006	0.168	0.226	0.826
MT	0.000	0.001	- 0.210	- 0.319	0.757

shows the effect of methanol to FFA in waste palm oil molar ratio, reaction time (T), on the FFA and Fig. 2c

shows the effects of acid catalyst amount and reaction time on the FFA. Fig. 2 presents the limit values of the optimum values in reducing FFA to lower than 2% wt.. They indicate that amount of acid catalyst (H_2SO_4) are 4.5-5.6% (wt./wt.) of FFA in WPO and 80-120 min of reaction time. Methanol should be used between

Fig. 1 Correlation coefficient (R^2) determined from the regression model of esterification step of waste palm oil.

23 to 28 mol of methanol to FFA in WPO molar ratio which is obtained from the RSM.

3.4 Model Development for Esterification Step

The model was developed to predict optimization of esterification step by using optimization function of the SPSS Software [5]. The five conditions were selected from the optimum values in reducing FFA to lower than 2% wt. from response surface plot (Fig. 2) showed in Table 6. They were both experimental values and predicted values which indicated that the comparison of both value was good correspondence between them, empirical models derived from RSM can be used to describe the relationship between the factors and response in esterification step from WPO.

The prediction of the developed model showed that the optimized condition at 28 mol methanol to FFA in waste palm oil molar ratio, 5.5% H_2SO_4 for 90 min of reaction time could reduce FFA in WPO to lower than 2%. This condition was selected as the optimum condition because it could reduce FFA in WPO to 1.76% wt. which less than the other conditions, used less amount of acid catalyst. Comparing with the

condition of experiment (No. 5) in Table 6 that could reduce the FFA in WPO to 1.70%, but it used more amount of acid catalyst.

3.5 Transesterification Step and Biodiesel Properties

After the esterification step, the transesterification reaction was run with optimized condition at 12 mol methanol to esterified oil molar ratio, 1.5% KOH for 55 min of reaction time. Waste palm oil biodiesel with optimized condition in two-step catalyzed process gave methyl ester content at 84.05% according to EN 14103

Fig. 2 Response surface plots representing the effect of factors on FFA predicted from the quadratic polynomial model.

Table 6 Optimized conditions of esterification step by RSM.

Experiment No.	Optimized condition			FFA (%)	
	M (mole)	C (%wt./wt.)	T (min)	Experimental	Predicted
1	27	5.4	90	1.92	1.87
2	27	5.5	90	1.90	1.82
3	28	5.3	90	1.91	1.85
4	28	5.5	90	1.76	1.73
5	28	5.6	90	1.70	1.69

Table 7 The physical and chemical properties of waste palm oil methyl ester.

Properties	Unit	Waste palm oil biodiesel (FAME)	Thai community biodiesel standard	ASTM D 6751	EN 14214
Density at 15 °C	g/cm ³	0.860	0.86-0.9	-	0.86-0.96
Viscosity at 40 °C	cSt	4.57	1.90-8.0	1.96-6.0	3.50-5.00
Flash point	°C	171	120 min	120 min	130 min
Acid value	mg KOH/g	0.78	0.80 max	0.80 max	0.50 max
Water and sediment	% mol	< 0.05	0.02 max		

method. The properties of waste palm oil methyl ester were shown in Table 7. They met the standards of Thai community biodiesel that can be used as fuel in agricultural machine.

4. Conclusions

The WPO with high FFA (48.62% of FFA) could be used as raw material to produce biodiesel. The FFA in WPO can be reduced to less than 2% by optimizing the CCD and RSM in the esterification step. The optimum conditions of esterification reaction were obtained at 28 mol of methanol to FFA in WPO molar ratio, 5.5% sulfuric acid concentration in 90 min of reaction time and 60 °C of reaction temperature. After the optimum conditions were determined, the transesterification step was carried out with alkaline catalyst to produce biodiesel. The result gave methyl ester content at 84.05% according to EN 14103 method. The properties of waste palm oil methyl ester met the standards for community biodiesel of Thailand.

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References

- [1] Meher, L. C., Sagar, D. V. and Naik, S. N. 2006. "Technical Aspects of Biodiesel Production by Transesterification-a Review." *Renewable Sustainable Energy Reviews* 10 (3): 248-68.
- [2] Ramadhas, A. S., Muraleedharan, C. and Jayaraj, S. 2005. "Performance and Emission Evaluation of a Diesel Engine Fueled with Methyl Esters of Rubber Seed Oil." *Renewable Energy* 30 (1): 789-800.
- [3] Ramadhas, A. S., Jayaraj, S. and Muraleedharan, C. 2004. "Use of Vegetable Oils as I.C. Engine Fuels - a Review." *Renewable Energy* 29: 727-42.
- [4] Omar, W. N. N. W. and Amin, N. A. S. 2011. "Optimization of Heterogeneous Biodiesel Production from Waste Cooking Palm Oil via Response Surface Methodology." *Biomass and Bioenergy* 35: 1329-38.
- [5] Guru, M., Artukonglu, B. O., Keskin, A. and Koca, A. 2009. "Biodiesel Production from Waste Animal Fat and improvement of Its Characteristics by Synthesized Nickel and Magnesium Additive." *Energy conversion and Management* 50: 498-502.
- [6] Jeong, G. T., Yang, H. S. and Park, D. H. 2009. "Optimization of Transesterification of Animal Fat Ester Using Response Surface Methodology." *Bioresour Technol* 100: 25-30.
- [7] Vicente, G., Coteron, A., Martinea, M. and Aracil, J. 1998. "Application of the Factorial Design of Experiments and Response Surface Methodology to Optimize Biodiesel Production." *Industrial Crops and Products* 8: 29-35.
- [8] Bhatti, H. N., Hanif, M. A., Qasim, M. and Rehman, A. 2008. "Biodiesel Production from Waste Tallow." *Fuel* 87: 2961-66.