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OPTIMIZATION OF ETHYL ESTER PRODUCTION FROM PALM OIL

K. Noipin*, S. Kumar

Energy Field of Study, School of Environment, Resources and Development,
Asian Institute of Technology, P.O. Box 4, Klong Luang, Pathumthani 12120, Thailand

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Abstract

This study presents the development and optimization of the KOH-catalyzed synthesis, transesterification reaction, of fatty acid ethyl ester from palm oil by factorial design and response surface methodology. The variables considered were ethanol/oil molar ratio, reaction temperature and catalyst concentration by weight of palm oil and the responses were ethyl ester yield. Catalyst concentration was found to be the most important factor and has negative effect on ethyl ester yield, while reaction temperature is the second factor of significance with negative effect on ethyl ester yield, due to yield losses caused by soap formation from saponification-side reaction and ethyl ester dissolution in glycerin. Second-order models were obtained to predict the responses analyzed as a function of the three variables and were found to describe the experimental ranges studied adequately.

Keywords: Biodiesel; Palm oil; Fatty acid ethyl esters; Optimization; Factorial design.

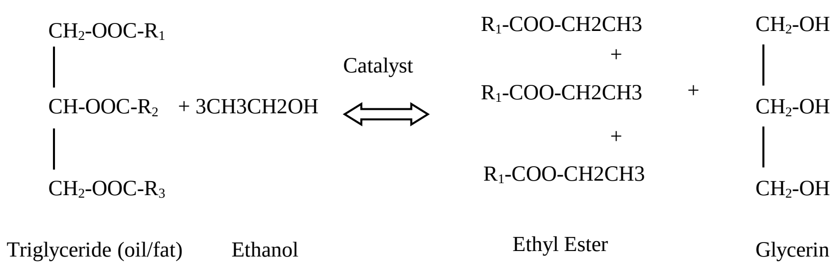
1. Introduction

Increase in the consciousness about the protection of environment especially due to climate change caused by GHG emissions and the conservation of non-renewable natural resources has led to various approaches, such as, energy efficiency, energy saving, adaptation, and renewable energy promotion. Using renewable energy resources is one key measure to mitigate the above noted problems, and has given rise to the alternative development of sources of energy as substitutes to conventional fossil fuels.

46% of all liquid fuel consumption of Thailand in 2009 was diesel [1], as it fuels a major part of the transportation sector. One of the most potential substitutes to diesel fuel is biodiesel.

Biodiesel is obtained from renewable resources and is also biodegradable. It has lower emissions than petroleum-based diesel and reduces the amount of net greenhouse gases or sulfur to the atmosphere [2-3]. Biodiesel is synthesized by transesterification of vegetable oils or animal fats with alcohol, and commonly methanol is used for commercial biodiesel. So, the most common form of biodiesel is methyl ester [4].

One of disadvantages of methanol derived biodiesel is that most methanol used today are produced from petroleum industry. It is highly toxic and can be absorbed through the skin. Besides, it is 100% miscible with water, and so any spill can lead to serious dangers [5]. Therefore, ethanol derived from agricultural raw material is an interesting option to be considered to produce biodiesel. The transesterification reaction can be represented as:



Glycerin is also obtained as a by-product similar to that from methyl ester production, and has applications in cosmetics, pharmaceutical, food and plastics industries.

Palm oil as raw material for biodiesel production is an interesting option since it is the largest component of global vegetable oil production (36% in 2009). Palm is an all year round plant and gives high amount of oil yield in comparison with other oily plants, for example, the oil yield of palm, soybean, sunflower, rapeseed and coconut are 5,940; 449, 954; 1,188 and 2,685 liter/hectare, respectively [6].

Generally biodiesel produced by transesterification of palm oil and methanol, called methyl ester, is suitable for using as fuel for diesel vehicles. Therefore, palm oil is a promising oil feedstock for biodiesel production in Southeast Asia, as it grows well in this region. For example, Indonesia and Malaysia were the world's top two producers of palm oil in 2008/09. The Malaysian government introduced the National Biofuel Policy in 2005 for the production of biodiesel from palm oil for use in the transport and industrial sectors [7].

Biodiesel production and characterization [8-12], and optimization by factorial design methodology for biodiesel production have been previously studied [13-14]. In the production of methyl ester from sun flower oil, it was found that temperature and catalyst concentration have a positive influence on ester yield [15], while waste cooking oil can also produce biodiesel, where catalyst concentration is the most important factor, but which has a negative influence on biodiesel yield and a positive influence on ester purity [16]. In case of ethyl ester production, optimization for biodiesel production from sunflower oil and Ethiopian mustard oil has been done, and the effects of reaction variables on ester yield depend on oil composition [5]. The effect of ethanol-palm kernel oil ratio on biodiesel yield has been studied [17], however, there has been no significant work done on the optimization by factorial design and oil characterization of ethyl ester from palm oil. The effects of various parameters on ethyl ester yield from palm oil such as reaction temperature, oil to ethanol molar ratio, and catalyst concentration are not available, as well as the optimum conditions for ethyl ester production.

In the present work, evaluation of the different variables affecting the transesterification process of palm oil and ethanol with alkaline catalyst were investigated. The optimum condition of biodiesel production process was determined by application of factorial design of experiments and response surface methodology from which interactions among experimental variables within the range of the study parameters can be seen, and this can help reducing time and cost [18]. The products were also characterized and their properties were compared to Thai biodiesel specification, focusing on the specification of community biodiesel of Thailand, which is the specification for biodiesel focusing on the use for low speed diesel engine.

2. Method

Ethyl ester was synthesized from transesterification reaction of palm oil and ethanol in a wide range of reaction temperature (40-75^{O}C), ethanol/oil molar ratio (6:1-18:1), and catalyst concentration (0.4-2.0 wt.%) to evaluate the effect of reaction parameters on ethyl ester yield. The optimum condition of production process was determined by statistical analysis using factorial design and response surface methodology (RSM). The response surface methodology explores the relationships between several independent variables and one or more response variables which are shown by two and three-dimensional plots. In this study, independent variables are ethanol/oil molar ratio, reaction temperature and catalyst concentration, while the response variable is ethyl ester yield.

2.1. Equipment

Experiments were conducted in a 5 L batch reactor (three-necked round bottom flask) with mechanical stirring, provided with a reflux condenser to avoid ethanol losses. The reaction temperature was kept constant throughout the reaction by immersing the reactor in a thermostatic bath. The reaction temperature was controlled and varied.

2.2. Materials

Refined palm oil was supplied by Patum Vegetable Oil Co.,Ltd, with total acid number of 0.6 mgKOH/g and its chemical composition is as follows: Oleic acid (C18:1) 46.6%, Palmitic acid (C16:0) 36.5% and Linoleic acid (C18:2) 12.0%. Ethanol of 99.8-99.9% purity was supplied by Labscan Asia Co.,Ltd. The catalyst used was potassium hydroxide (85%) purity from Labscan Asia Co.,Ltd.

2.3. Experimental Procedure

Experimental conditions were considered by using factorial design methodology. The conditions for fatty acid ethyl ester production were varied using palm oil as raw material to find the condition for fatty acid ethyl ester production such as ethanol/oil molar ratio, reaction temperature, and catalyst concentration. The values of each variable for synthesis conditions were selected based on the optimum conditions of previous research works [4-5,16]. From literature, each methyl ester or ethyl ester production resulted in different optimal conditions and molar ratio, temperature, and catalyst concentration of ethyl ester production were therefore selected from these conditions and covered the lower and upper values of the conditions found in the literature. Thus, oil-to-ethanol molar ratio was studied in the range between 1:06 and 1:18 ratio, and the chosen catalyst concentration levels were 0.4 and 2.0 wt.% [5,16]. Temperature levels were selected by considering the reactant properties and literature review [4,16], from 40 to 75^{O}C.

The experiments of ethyl ester production were carried out by the following procedure: Vegetable oil was added into the reactor, round bottom flask fitted with a reflux condenser to avoid ethanol losses. The catalyst was diluted in ethanol by using mechanical agitation assistant. When the set temperature was reached, the mixture of catalyst and ethanol was fed into the reactor. Then, the reaction mixture was stirred during the total reaction time of 5,400 seconds (1.5 hours).

The product was cooled and distilled to remove excess ethanol followed by separation process using separating funnel. It was separated into two layers, the upper ethyl ester (biodiesel) layer and the lower glycerin layer. The produced biodiesel then washed with water until the washing was neutral.

During each experiment, the following variables were kept constant: pressure, reaction time and impeller speed. After the experiments, samples of the products were analyzed by gas chromatography and ethyl ester yields were observed. [4-5,15]

2.4 Statistical analysis

The experimental conditions of ethyl ester synthesis by transesterification of palm oil using KOH as catalyst were determined by factorial design of experiments. There are usually multiple factors involved and it is important to consider them together in case they interact or influence each other. This is done using a full factorial design of experiments. There are 2^3 or 8 experiments for the case of 3 factors in this study and amplified to response surface methodology (RSM). The factors selected were oil-to-ethanol molar ratio, reaction temperature and catalyst concentration. The factors were selected by considering the fact that they are the reaction parameters easily controlled by operators within local communities. The impeller speed was fixed at 600 rpm in order to avoid mass transfer limitation and the reaction time was 5,400 seconds (1.5 hours).

There are two main levels for each factor, high level or maximum value of variable range (coded 1) and low level or minimum value of variable range (coded -1), and the middle level or middle value of variable range or centerpoint (coded 0) was set in order to estimate experimental error, as shown in Table 1.

Table 1 Values of the considered factors for each level

Variable	Minimum coded value (-1)	Middle coded value (0)	Maximum coded value (1)
Ethanol/Oil Molar Ratio (R)	6:1	12:1	18:1
Reaction Temperature (T)	40	57.5	75
Catalyst Concentration (C)	0.4	1.2	2

In case of coded design levels, *X*R is the coded number of oil-to-ethanol molar ratio. *X*T is for reaction temperature and *X*C is for catalyst concentration. The response selected, *Y*, was the yield of ethyl ester as shown in Table 2.

2.5 Product characterization

The fuel characteristics of the synthesized ethyl esters were determined according to ASTM standard methods as follows:
(i) Density at 15 ^{O}C (ASTM D4052), (ii) Viscosity at 40 ^{O}C (ASTM D445), (iii) Flash point (ASTM D93), (iv) Gross Heat of Combustion (ASTM D240), and Pour point (ASTM D97).

Table 2 The experimental matrix and experimental results for the 2^3 factorial design

Run	Variables			Coded Design Levels			Yield; *Y* (%)	
	R	T (^{O}C)	C (wt.%)	*XR*	*XT*	*XC*	Replicate1	Replicate2
1	6:1	40	0.4	-1	-1	-1	86.57	88.12
2	18:1	40	0.4	1	-1	-1	90.58	91.73
3	6:1	75	0.4	-1	1	-1	82.25	82.98
4	18:1	75	0.4	1	1	-1	89.28	88.89
5	6:1	40	2	-1	-1	1	71.58	76.08
6	18:1	40	2	1	-1	1	60.15	66.99
7	6:1	75	2	-1	1	1	27.87	32.78
8	18:1	75	2	1	1	1	56.98	62.23
9	12:1	57.5	1.2	0	0	0	82.57	79.23
10	12:1	57.5	1.2	0	0	0	77.86	77.45
11	12:1	57.5	1.2	0	0	0	79.15	82.18
12	12:1	57.5	1.2	0	0	0	82.23	84.33

3. Observations and Results

3.1. Process optimization

Table 2 shows the experimental matrix and experimental results for 2^3 factorial design, three factors and each run at two levels. Real levels and coded factor levels (±1) for the three factors are given on column 2-7. The last two columns show the conversion to ethyl ester (yield) obtained from each run. Four additional experiments (last four rows of the matrix) were carried out at the center-point level, coded as '0', to estimate experimental error. There are 12 experiments for 2^3 factorial design and two replicates were done. In total, 24 experiments were carried out.

Statistical analysis was carried out using these experimental values, and the three main effects and four interaction effects were estimated. The analysis of the main effects and interaction effects for the chosen response in Table 3 shows that the three main effects and three interaction effects are significant. Significance of each effect is considered from probability value (p-value). The p-value was fixed at 0.05 or 5% (confidence level of 95% in this study). In the analysis, p-value of each effect was calculated and the effect that gives p-value less than 0.05 has significant effect. On ethyl ester yield, the three main effects, ethanol to oil molar ratio (R), reaction temperature (T), and catalyst concentration (C) are significant. In case of interaction effects, only ethanol to oil molar ratio – catalyst concentration interaction is not significant. Besides, catalyst concentration effect is larger than ethanol to oil molar ratio effect and temperature effect.

Table 3 Statistical analysis for the 2^3 factorial design

Number of experiments:	8	Degrees of freedom:	7
Response	Ethyl Ester Yield (%)		
Main effects and interaction effects:	Ethanol/oil molar ratio effect, R = 7.32 Reaction temperature effect, T = -13.57		
	Catalyst concentration effect, C = -30.72		
	Ethanol/oil molar ratio-reaction temperature interaction effect, RT = 10.55		
	Ethanol/oil molar ratio-catalyst concentration interaction effect, RC = 2.18		
	Reaction temperature-catalyst concentration interaction effect, TC = -10.17		
	Ethanol/oil molar ratio-reaction temperature-catalyst concentration interaction effect, RTC = 9.22		
	Significance test:		
Confidence level	95%	Standard deviation, S	5.279
Significant effect	R,T, C, RT, TC, RTC		
Response equation:	$Y = a_0 \sum_{k=1}^{3} a_k X_k + \sum_{k=1}^{3} a_{kk} X_k^2 + \sum_{k \neq j}^{3} a_{kj} X_k X_j$		

The negative values of main effects and interaction effects in Table 3 mean that the higher of the values, the lower of the ethyl ester yields. On the other hand, positive values mean that the higher of the values, the higher of the ethyl ester yields.

The use of factorial design of experiments and analysis assisted by Minitab software provided a polynomial model for predicting the amount of ester yield. We can write the response, yield of ester, as a function of the significant factors and the best-fitting response surface can be written as follows.

Statistical model

$$Y = 80.63 + 3.66X_R - 6.78X_T - 15.36X_C - 8.43X_R^2 + 5.28X_{RT} - 5.08X_{TC} \text{ (r = 0.93)} \quad (1)$$

Technological model

$$Y = 97.78 + 3.07R - 0.55T - 1.05C - 0.23R^2 + 0.05RT - 0.36TC \quad \text{(r = 0.93)} \quad (2)$$

From equation (1) and (2), X_T, X_C, X_R, X_{RT}, and X_{TC} are coded values (±1) of factor levels while T, C, R, RT, and TC are real values of factor levels.

The statistical model is obtained from coded levels giving the real influence of each variable on the process and the technological model from the real values of the factor levels. Equations (1) and (2) are only valid within the experimental ranges considered. The second-order model can be plotted as a three-dimensional surface and contour plots representing the response as a function of main effects and interaction effects, which show the ester yield for experimental range of the parameters (see Figure 1-4). Figure 1 illustrates the response surface for the predicted values of the ethyl ester yield as a function of catalyst concentration and reaction temperature using palm oil with ethanol to oil molar ratio of 12:1. It is found that ethyl ester yields are high with low catalyst concentration and very low with high catalyst concentration especially with both high catalyst concentration and high reaction temperature.

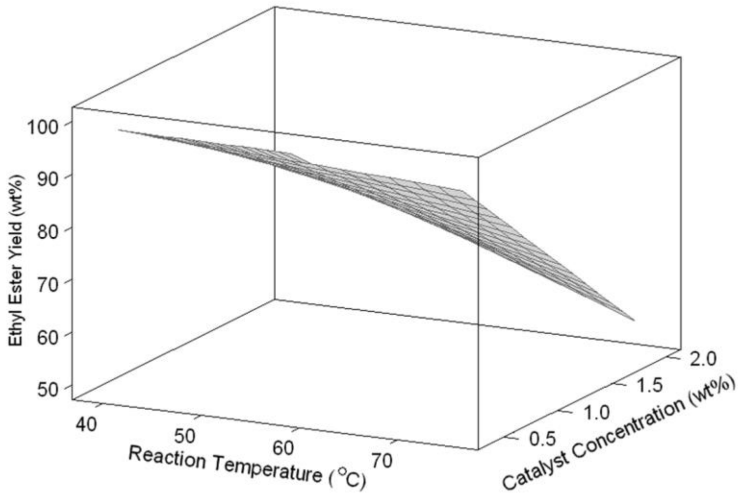


Figure 1. Response surface of ester yield vs. reaction temperature and catalyst concentration for the second-order model with ethanol to oil molar ratio of 12:1

In addition, the model obtained for the response can be represented in two-dimensional graphs called plots in order to determine the effect of the parameters on ethyl ester yield for the process.

The contour plots represented in Figure 2-4 illustrate the effect of reaction parameters on ethyl ester yield within the experimental ranges considered. These response surface and contour plots are very useful for visualization of the reaction system or how parameters affect ethyl ester yield. Figure 2 represents the contour plots for ethyl ester yield as a function of reaction temperature and catalyst concentration at ethanol to oil molar ratio of 12:1. The operating conditions with the highest production yield of 95% are at 0.5%wt of catalyst concentration and reaction temperature of around 45-65 ^{O}C. It is found that reaction with high catalyst concentration and high reaction temperature should be avoided because of low production yield. It is probably caused by soap formation from saponification reaction in such conditions.

Figure 3 shows the contour plots for these responses as a function of ethanol to oil molar ratio and catalyst concentration at the reaction temperature of 57.5^{O}C. The operating conditions with the highest production yield of 95% are at catalyst concentration of around 0.5%wt and ethanol to oil molar ratio of around 11:1 to 14:1. As shown in the figure, the process with high catalyst concentration should be avoided since ethyl ester yield is quite low.

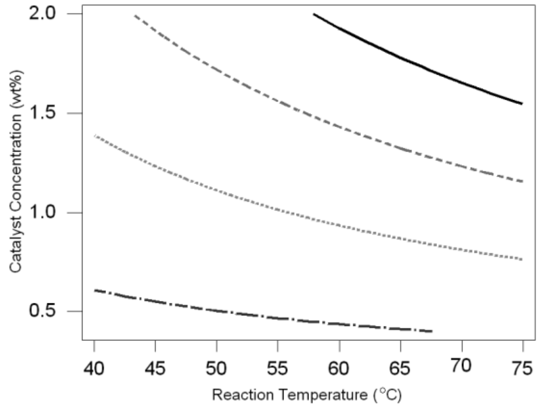


Fig. 2. Contour plots of ester yield vs. reaction temperature and catalyst concentration for the second-order model with ethanol to oil molar ratio of 12:1

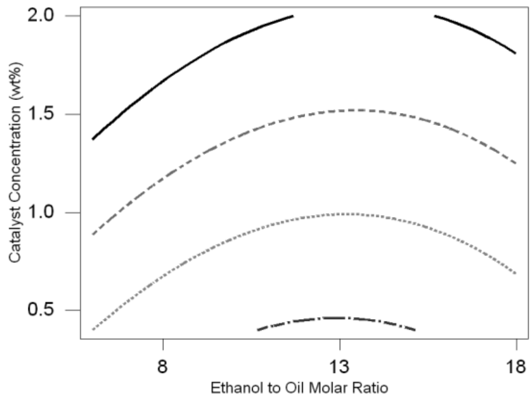


Fig. 3. Contour plots of ester yield vs. ethanol to oil molar ratio and catalyst concentration for the second-order model with reaction temperature of 57.5°C

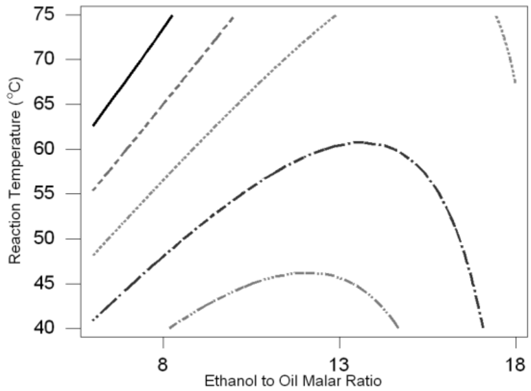


Fig. 4. Contour plots of ester yield vs. ethanol to oil molar ratio and reaction temperature for the second-order model with catalyst concentration of 1.2%

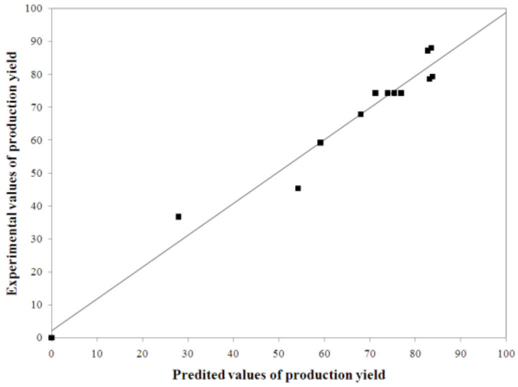


Figure 5. Comparison of experimental vs. predicted values of the ethyl ester production

———— 65% yield – – – – – 75% yield .... 85% yield — · — 95% yield

Finally, Figure 4 shows the contour plots for ethyl ester yield as a function of ethanol to oil molar ratio and reaction temperature at the catalyst concentration of 1.2%. The operating conditions with the highest production yield of 85% are at reaction temperature of around 40 to 45 ^{O}C and ethanol to oil molar ratio of 8:1 to 14:1. The production yield is quite low in high reaction temperature conditions.

As seen in Figures 3 and 4, with the same trend with that of Figure 2, ethyl ester synthesis with high catalyst concentration and high reaction temperature should be avoided. That is because of saponification reaction occurring during production process.

4. Discussion

4.1 Influence of main effect

From ethanol boiling point and literature review, a molar ratio range of ethanol to palm oil from 6:1 to 18:1 was examined. Determined by statistical analysis, the ethanol/oil molar ratio is a significant effect and it has a positive influence on transesterification of palm oil since the effect value from statistical analysis is 7.32 as shown in Table 3, which means that ethyl ester yield increases with increasing of ethanol/oil molar ratio.

Catalyst concentration is the most significant factor on the transesterification process of palm oil and ethanol. It has a negative influence on the response, which means that ethyl ester yield decreases with increasing of catalyst concentration. It is caused by the fact that an increase in the amount of the catalyst increases the amount of soap produced through saponification reaction. The produced soap dissolves in the glycerin layer and hence ethyl ester solubility in glycerin increases. As a result, the ethyl ester yield decreases [5,13,16].

Reaction temperature also has a negative effect for ethyl ester production. This is presumably due to saponification reaction occurring during the process that produces soap as well.

4.2 Influence of interaction effect

Reaction temperature-catalyst concentration (T-C) is significant and has a negative influence on the experimental ranges considered which is caused by by-product, soap formation from saponification reaction, so ester yield decreases.

Ethanol/oil molar ratio-reaction temperature (R-T) interaction has a statistically significant positive influence on the transesterification reaction of palm oil and ethanol.

Ethanol/oil molar ratio-catalyst concentration (R-C) interaction has a positive influence on the process but it is not significant.

Ethanol/oil molar ratio-reaction temperature-catalyst concentration (R-T-C) interaction is significant and its influence on the process is positive.

It can be seen that R-T, R-C, and R-T-C interaction have a positive effect on production yield. From the fact that percentage of conversion would be high in the presence of excess amount of alcohol molecules for transesterification reaction of triglyceride, higher ethanol/oil molar ratio should gives high production yield since theoretical molecular ratio of alcohol to oil for biodiesel production is 3:1. Furthermore, higher reaction temperatures provide more energy for transesterification activity but, as mentioned earlier, reaction with both high reaction temperature and high catalyst concentration give low production yield due to soap formation.

4.3 Analysis of response surface

Figures 1-4 show the response surface and contour plot corresponding to ester yield versus reaction temperature and catalyst concentration which indicates that for both low and high temperatures, ethyl ester conversion increases with decreasing catalyst concentration. Maximum ester yield is achieved at low catalyst concentration level and wide range of reaction temperature. This is due to the fact that catalyst concentration is the most significant factor but its effect is negative.

Since the reaction temperature effect is negative and smaller than that of the catalyst concentration, at high catalyst concentrations, there is a moderate decrease in ester conversion with reaction temperatures and at low catalyst concentrations only very small changes in ester conversion with reaction temperatures can be observed. Soap formation from saponification reaction is an undesirable side reaction which diminishes ethyl ester yield. Hence, from the response surface, large catalyst concentration and large reaction temperature should be avoided in order to keep away from soap formation.

The plot of experimental values versus predicted values for ethyl ester production from palm oil is shown in Figure 5. It can be observed that the model explains the experimental ranges studied adequately.

Reaction conditions for biodiesel production giving high production yield mainly depend on composition of oil/fat and alcohol used. For example, the production of biodiesel from sunflower oil and methanol with 97% of yield can be achieved at mild reaction temperature (20-50^{O}C) and catalyst concentration of 1.3wt.% [15]. Biodiesel production from jatropha oil and methanol with 90-95% of yield can be achieved at 60^{O}C of reaction temperature, 9:1 of ethanol/oil molar ratio and 2% of catalyst concentration [19]. From the model in this study, the highest yield is 91% at 40^{O}C of reaction temperature, 10:1 of ethanol/oil molar ratio and 0.5% of catalyst concentration.

4.4 Ethyl ester characteristics

Some of the most important quality parameters of biodiesel produced in the experiments are shown in Table 4. These parameters were compared with biodiesel standards of Thailand, specification of community biodiesel and (commercial) biodiesel.

In all cases, density and flash point met the specification of community and commercial biodiesel. Nonetheless, viscosity parameters of the products were within the specification of community biodiesel for all production conditions, but were out of specification of commercial biodiesel for the experimental conditions of Run 1 and Run 3, as well as the results of ethyl ester yields.

Table 4 Properties of the produced ethyl ester from palm oil for each synthesis condition

Property		Density at 15 ^{O}C (kg/m^3)	Viscosity at 40 ^{O}C (m^2/s)	Flash point (°C)	Gross heat of combustion (J/g)	Pour point (°C)	Ethyl ester content (%wt.)
Run[c]	1	873.1	0.0000052	181.5	40,109	9	94.6
	2	870.9	0.0000048	181.5	40,261	6	98.25
	3	873.9	0.0000053	179	40,193	9	89.4
	4	871.1	0.0000048	179.5	40,313	6	96.7
	5	870.3	0.0000047	175.5	40,249	6	98.45
	6	870.1	0.0000047	180	40,220	9	97.4
	7	870.5	0.0000048	180.5	40,170	9	98.4
	8	870.2	0.0000047	180.5	40,423	6	99.75
	9	870.5	0.0000048	179	40,308	9	99.25
	10	870.6	0.0000048	177	40,468	9	98.85
	11	870.5	0.0000048	172	40,226	9	97.1
	12	870.6	0.0000048	175.5	40,270	9	98.2
Limits 1[a]		860 – 900	0.0000019 – 0.000008	> 120	-	-	-
Limits 2[b]		861 – 900	0.0000035-0.000005	> 120	-	-	>96.5

[a] Specification of community biodiesel of Thailand; [b] Specification of biodiesel of Thailand (Commercial Biodiesel); [c] Conditions of each experiment run are shown in Table 2

Excluding both biodiesel specifications, heating value and pour point were also determined. Gross heat of combustion or heating value, one of the main factors that affect vehicle fuel economy, torque, and horsepower, indicates energy content or the heat released when a known quantity of fuel is burned under specific conditions. Heating values for all conditions are very similar.

Pour point indicates the capability of biodiesel utilization in cold weather because it is the lowest temperature that biodiesel can be poured by gravity [20]. From the results, it is clear that the products can be used very well especially in tropical area. In case of ester content, the limit is specified only for commercial biodiesel and the values of most of the products produced in this study are within the limit.

In addition, the fuel property analysis of the product was done in detail relevant to the specification of community biodiesel of Thailand, as shown in Table 5. The tested product was produced from the optimum process, reaction temperature of 60 ^{O}C, catalyst concentration of 0.5%, molar ratio of 10:1, which is considered from %yield, %ethyl ester, resource consumption, and available equipment. It is found that all fuel properties of the products are within the limits of the specification of community biodiesel of Thailand. Thus, ethyl ester from palm oil can be used as fuel effectively especially for community level or low speed diesel engine.

From Table 5, the properties of the product in this study were also compared with those of biodiesel produced from other kinds of oil. It is found that the results of this study are very satisfactory. For example, density test results of all case studies are similar but viscosity of waste palm oil ethyl ester (WPEE) [21] case study is very high especially out of the specification of community biodiesel. It means that the product is too thick to be used in diesel engines since it can be the cause of engine damage. In case of rapeseed ethyl ester (REE) [22] case study, flash point test result is quite low. Flash point is useful in terms of safety aspect for fuel use especially in hot weather. For CME case study with flash point of 109^{O}C, the fuel is quite dangerous to use because it can ignite easily. The sulfur content that has a serious impact to environment is a strict item for fuel use in diesel engines and the test results show results that are very satisfactory compared with other studies. In summary, the properties of the product in this study are within the limits for all parameters.

Table 5 Fuel properties of ethyl ester from palm oil comparing to the specification of community biodiesel of Thailand and the results in the literatures

Property, Unit	Unit	Result from this study	Limits of community biodiesel	HOSO[a] [5]	REE[b] [22]	WPEE[c] [21]	Test Method
Density at 15.0 °C	kg/m^3	872.3	860 – 900	850	876	874	ASTM D4052
Viscosity at 40 °C	mm^2/s	4.9	1.9 – 8	4.9	6.2	15 (at 20°C)	ASTM D445
Flash point	°C	182.5	> 120	-	124	-	ASTM D93
Sulfur content	%wt.	0.0001	< 0.0015	-	0.014	0.18	ASTM D5453
Sulfated ash	%wt.	<0.001	< 0.02	-	-	-	ASTM D874
Water and Sediment	%vol.	<0.025	< 0.2	500 (mg/kg)	-	-	ASTM D2709
Copper strip corrosion	Number	1a	< No.3	-	-	-	ASTM D130
Total acid number	mgKOH/g	0.27	< 0.80	0.08	-	-	ASTM D664
Free glycerin	%wt.	<0.005	< 0.02	0.002	-	-	EN 14105
Total glycerin	%wt.	0.552	< 1.5	0.002	-	-	EN 14105

[a]High oleic sunflower oil ethyl ester ;[b]Rapeseed ethyl ester;[c]Waste palm oil ethyl ester

5. Conclusions

In the present study, process optimization of ethyl ester production from palm oil using KOH as a catalyst was performed by factorial design of experiment and response surface methodology. A full two-factorial design is a very useful tool in the study of the influence of the variables on the process.

The study of the parameters affecting the responses shows that, within the experimental ranges considered, reaction temperature and catalyst concentration were found to have a negative influence on the ethyl ester yield and catalyst concentration is the most important factor. This is due to side reaction like soap formation and ethyl ester dissolution in glycerin. The reaction conditions with high reaction temperature (>60 °C) and catalyst concentration (>1.5%) should be avoided because of large amount of soap produced during the process. High ethyl ester conversion can be obtained at small amount of catalyst, around 0.5-0.8%, and wide range of temperature of 55-75 °C.

Response equations have been obtained to predict the yield of ethyl ester and a function of ethanol/oil molar ratio, reaction temperature, and catalyst concentration. These second-order models are useful to determine the optimum conditions for the study using the minimal number of experiments and it is found that the models describe the experimental ranges studied adequately.

Acknowledgments

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*Corresponding author. Tel.: 66 35 248190, E-mail address: Kate-Natee.Noipin@ait.ac.th (K. Noipin)