Enhancement of Biodiesel Production from Palm Fatty Acid Distillate Using Methyl T-Butyl Ether Co-Solvent: Process Optimization

Ruamporn Nikhom*[‡], Chokchai Mueanmas*, Kittiphoom Suppalakpanya**

* Faculty of Engineering, Thaksin University, Phattalung, 93210, Thailand

** Faculty of Agro Industry, Rajamangala University of Technology Srivijaya, Nakhon Si Thammarat, 80240, Thailand

(ruamporn6798@gmail.com, cmueanmas@hotmail.com, kit_src@yahoo.com)

[‡] Corresponding Author; Ruamporn Nikhom, Energy Engineering Program, Faculty of Engineering,
Thaksin University, Phattalung, 93210, Thailand,

Tel: +667 460 9600 Ext. 3602, ruamporn6798@gmail.com

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Abstract- Biodiesel production from a non-edible feedstock, palm fatty acid distillate (PFAD), in the presence of methyl t-butyl ether (MTBE) co-solvent was investigated. The reaction conditions were optimized in terms of their effect on free fatty acid (FFA) conversion by response surface methodology (RSM). The maximum FFA conversion of 98.93 wt.% was obtained at a molar ratio of methanol to FFA of 7:1, using 10 wt.% H_2SO_4 during a reaction time of 70 min with 25 wt.% of MTBE co-solvent. The addition of MTBE co-solvent increased the reaction rate of esterification and acid-catalyzed transesterification. As a result of the increased reaction rates, the amount of unreacted FFA and glycerides in the final product were lower than were found in the product of a co-solvent free system.

Keywords Biodiesel, Palm fatty acid distillate, Esterification, Co-solvent, Optimization, RSM.

1. Introduction

The current environmental situation and energy demand are driving the development of renewable energy in many countries [1,2], including Thailand. Fossil-based fuels today meet 85% of the world global energy consumption [3]. However, fossil fuels have a finite and possibly run out in a couple of decades [4]. Therefore, a new alternative sources to be powered internal combustion engines (ICEs) is required because today transportation is nearly entirely (>99.9 %) powered by ICEs [5]. Biodiesel is seen as a promising renewable energy source because it can be used directly or in combination with diesel fuel without major engine modification [6,7]. Moreover, compared with diesel fuel, the use of biodiesel reduces exhaust emissions such as total unburned hydrocarbons, carbon monoxide, particulate matter, and sulphur oxides and reduces carbon dioxide generation [8-12].

The production of biodiesel, however, is controversial because it uses edible oil as a feedstock. This puts biodiesel production in direct competition with the production of food [13,14], causing prices of the latter to rise [15,16]. Non-edible oils feedstock, such as used cooking oil [17-19], jatropha oil [20], linseed oil [21], and palm fatty acid distillate (PFAD) [22,23], can reduce biodiesel production costs and alleviate the food-fuel conflict [13,24,25].

PFAD is one of the potential alternative feedstocks for biodiesel production [23,26]. Generally, 3 to 5 wt.% of PFAD is separated as a by-product during the crude palm oil refining process [27]. Thailand is the third largest palm oil producer in the world [28] and also produces a large amount of PFAD. Although PFAD is used in the soap-making industry and as a raw material in the oleochemical industry, there is usually a surplus of PFAD and therefore the price is low. PFAD contains more than 80 wt.% of free fatty acid (FFA) and 5 to 15 wt.% of triglyceride [23,26,29,30]. This

Nomenclature

ANOVA	Analysis of variance
CCD	Central composite design
DEE	Diethyl ether
FFA	Free fatty acid
H_2SO_4	Sulfuric acid
ICEs	Internal combustion engines
MTBE	Methyl t-butyl ether
PFAD	Palm fatty acid distillate
RSM	Response surface methodology
THF	Tetrahydrofuran

composition implies a potential as feedstock for biodiesel production using esterification with methanol in the presence of acid catalysts [14,23].

The esterification of FFA with methanol produces methyl ester (biodiesel) and a by-product of water. The acid-catalyzed transesterification of large-branched triglycerides into methyl ester also occurs as a side reaction [31], with glycerol as the by-product. In both reactions, the methanol and oil phases (FFA and triglyceride) are insoluble. Hence, the rate of reaction is controlled by the mass transfer between the two phases [21,32]. Although a higher reaction temperature can improve the solubility of the two phases, solubility only increases by 2 to 3 wt.% with temperature increments of 10 °C [33]. Increasing the reaction temperature enough to produce a useful improvement inevitably increases energy consumption.

Therefore, researchers have evaluated other ways of improving the solubility of the reactants, such as the use of co-solvents [20,21,32,34,35]. The most suitable co-solvents used in biodiesel production were ethers especially tetrahydrofuran (THF) [36]. They were suitable because they contained the right balance of polar and nonpolar entities required to lower the interfacial surface tension between the methanol and oil phases [36]. THF co-solvent exerted a positive effect on the transesterification of jatropha oil [20] and linseed oil [21] by increasing the reaction rate to achieve a high biodiesel yield in a short reaction time. Transesterification using methyl t-butyl ether (MTBE) and diethyl ether (DEE) co-solvents achieved higher biodiesel yields than transesterification without a co-solvent [36-38]. Other co-solvents that had an effect on transesterification rates were acetone [39], hexane [34], and n-pentane [40]. In esterification, using toluene co-solvent with a solid catalyst increased the biodiesel yield while reducing the methanol required for the reaction [41]. Another advantage of co-solvents was that, together with methanol, they were easy to recover by distillation for reuse in the production process [35]. Although the addition of co-solvents increased the reaction rate, too much co-solvent could inhibit the reaction because of the dilution effect [42].

In light of the rare research into the use of co-solvents in the esterification of PFAD, the present work aimed to improve PFAD esterification by using an MTBE co-solvent. Response surface methodology (RSM) was used to evaluate the effects of reaction conditions on FFA conversion and to optimize the conditions for the production of PFAD biodiesel. In addition, some fuel properties of the final product were also evaluated.

2. Materials and Methods

2.1. Materials

PFAD was purchased from Chumporn Palm Oil Industry Public Co. Ltd., Thailand. The PFAD was a soft wax at room temperature with a light yellow colour, as seen in Fig.1. The chemical composition consisted of 93 wt.% FFA, 0.153 wt.% moisture and the rest was monoglycerides, diglycerides, triglycerides and traces of impurities. All the chemicals for esterification (commercial grade methanol (99.5%), analytical grade MTBE (99%) and H_2SO_4 (98%)) were obtained from Union Intraco Public Co., Ltd. Analytical grade sodium hydroxide (99.9%) and phenolphthalein, for determination of FFA, were obtained from Labchem, USA.

Fig. 1. Palm fatty acid distillate (PFAD)

2.2. Experimental methods

2.2.1. Esterification procedure

Esterification of the PFAD was performed in a 500 mL three-necked flat-bottom reactor. The reaction was magnetically stirred and heated in an oil bath. The flask was equipped with a reflux condenser to condense the evaporated methanol and MTBE back to the reactor and a thermometer to monitor the reaction temperature. In the typical reaction, 100 g of PFAD was placed into the reactor and mixed with the requisite amount of methanol, H_2SO_4 and MTBE loading. The reaction temperature was kept constant at 55 °C, which is close to the boiling point of the co-solvent [43], and the reaction mixture was stirred at 300 rpm for a designed reaction time. The esterified product was purified as follows. Methanol-MTBE was separated from the product by distillation, the product was washed with warm water to remove residual impurities and the water was then evaporated from the product at 120 °C for 30 min. The residual FFA in the final product was determined by titration in accordance with AOCS Ca 5a-40. The FFA conversion was calculated using Eq. (1):

$$FFA\ conversion\ (wt.\%) = \left(1 - \frac{A_o}{A_i}\right) \times 100 \qquad (1)$$

Where A_i is the initial FFA in PFAD feedstock and A_o the residual FFA in PFAD biodiesel.

2.2.2. Fuel properties analysis

The fuel properties of the final biodiesel produced at the optimal condition were evaluated using the following standard methods: ester content (EN 14103), residual glycerides (EN 14105), density (ASTM D1298), viscosity (ASTM D4450), sulfated ash (ASTM D874), flash point (ASTM D93), copper strip corrosion (ASTM D130), cetane number (ASTM D613) and water content (EN 12937).

2.3. Experimental Design

The reaction conditions for PFAD esterification using a co-solvent were optimized in terms of their effect on FFA conversion. The conditions were optimized using RSM based on a central composite design (CCD) with 5 levels, using 4 independent variables of molar ratio of methanol to FFA, amount of H_2SO_4, reaction time and amount of MTBE co-solvent. This design required 28 experiments comprising 16 factorial points, 8 star points, and 4 center points. The independent variables and their design values are listed in Table 1. The effect of each independent variable and its correlation with the FFA conversion response were explained by a quadratic polynomial equation presented in Eq. (2):

$$Y = b_0 \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i>j}^{k} \sum_{j}^{k} b_{ij} X_i X_j + e \quad (2)$$

Where Y is the response (FFA conversion), b_0 is the intercept, b_i is the linear coefficient, b_{ii} is the quadratic coefficient, b_{ij} is the interaction coefficient, X_i and X_j are the independent variables studied, k is the number of independent variables studied, and e is the random error.

Statistical analyses included multiple regression analysis, analysis of variance (ANOVA) and model validation was analyzed by RSM software.

Table 1. Independent variables and levels

Independent variable	**Symbol**	**Levels**				
		-α	**-1**	**0**	**+1**	**+α**
Molar ratio of methanol to FFA	X_1	2:1	4.5:1	7:1	9.5:1	12:1
H_2SO_4 amount (wt.%)	X_2	2	4	6	8	10
Reaction time (min)	X_3	20	45	70	95	120
MTBE amount (wt.%)	X_4	10	17.5	25	32.5	40

3. Results and Discussion

3.1. Model fitting and statistical analysis

In order to evaluate the optimal conditions for PFAD esterification, experiments were performed via CCD modelling technique. The observed and predicted responses for FFA conversion are shown in Table 2. The highest FFA conversion of 98.93 wt.% was obtained at run no. 18 (molar ratio of methanol to FFA of 7:1, amount of H_2SO_4 of 10 wt.%, reaction time of 70 min and amount of MTBE of 25 wt.%). The quadratic model, fitted to a response and 4 independent variables, is expressed in Eq. (3):

$$Y = 68.64 + 5.796X_1 + 0.480X_2 + 0.166X_3 - 0.179X_4 - 0.266X_1^2 + 0.02087X_2^2 - 0.00033X_3^2 + 0.0020X_4^2 - 0.07128X_1X_2 - 0.01397X_1X_3 + 0.00501X_1X_4 + 0.00009X_2X_3 + 0.000964X_2X_4 + 0.000224X_3X_4 \quad (3)$$

Where Y is the FFA conversion, X_1 is the molar ratio of methanol to FFA, X_2 is the amount of H_2SO_4, X_3 is reaction time and X_4 is the amount of MTBE.

Table 2. Central composite design (CCD) matrix with FFA conversion from experimental and predicted results

Run no.	**Molar ratio of methanol to FFA; X_1**	**H_2SO_4 (wt.%); X_2**	**Time (min); X_3**	**MTBE (wt.%); X_4**	**FFA Conversion**	
					Experimental	**Predicted**
1	2:1	6	70	25	86.22	87.58
2	4.5:1	4	45	17.5	92.68	92.40
3	4.5:1	4	95	17.5	95.90	95.45
4	4.5:1	4	45	32.5	92.01	91.77
5	4.5:1	4	95	32.5	95.47	94.99
6	4.5:1	8	45	17.5	94.86	94.12
7	4.5:1	8	95	17.5	97.63	97.19
8	4.5:1	8	45	32.5	93.83	93.54
9	4.5:1	8	95	32.5	97.31	96.78
10	7:1	2	70	25	97.37	97.46
11	7:1	6	20	25	95.76	95.95
12	7:1	6	70	10	98.42	98.96
13	7:1	6	70	25	98.17	98.17
14	7:1	6	70	25	98.16	98.17
15	7:1	6	70	25	98.14	98.17
16	7:1	6	70	25	98.21	98.17
17	7:1	6	70	40	98.11	98.29

Run no.	Molar ratio of methanol to FFA; X_1	H_2SO_4 (wt.%); X_2	Time (min); X_3	MTBE (wt.%); X_4	FFA Conversion	
					Experimental	Predicted
18	7:1	10	70	25	98.93	99.55
19	7:1	6	120	25	98.21	98.75
20	9.5:1	4	45	17.5	98.47	98.61
21	9.5:1	4	95	17.5	98.21	98.17
22	9.5:1	4	45	32.5	98.24	98.35
23	9.5:1	4	95	32.5	97.73	98.08
24	9.5:1	8	45	17.5	98.75	98.90
25	9.5:1	8	95	17.5	98.63	98.48
26	9.5:1	8	45	32.5	98.65	98.70
27	9.5:1	8	95	32.5	98.50	98.45
28	12:1	6	70	25	96.09	95.45

According to the analysis of variance of the regression model in Table 3, a very small p-value of 0.00001 shows a very high significance that is adequate to represent the actual relationship between FFA conversion and the independent variables. The significance of the regression model was confirmed according to F-test with 95% confidence by an F-value was greater than its critical value F(0.05,14,13) [44]. Moreover, the correlation coefficients (R^2) of 0.975 was very close to the adjusted correlation coefficients (Adj. R^2) of 0.949 that also confirm the excellent accuracy of the regression model.

Table 3. Analysis of variance (ANOVA) for the regression model of PFAD esterification using a co-solvent

Source	Sum of squares	Mean sum of squares	F-value	P-value Prob> F	Degrees of freedom
Regression	204.13	14.58	36.71	<0.00001	14
Residual	5.164	0.397			13
LOF Error	5.161	0.516	598.8030	0.000101	10
Pure Error	0.00259	0.000862			3
Total	209.29				27

Note: $R^2 = 0.975$, Adj. $R^2 = 0.949$, F(0.05,14,13) = 2.557

3.2. Response surface plots for PFAD esterification using a co-solvent

Surfaces plots are an easy and convenient way to understand the interaction between two reaction parameters and also to locate their optimum levels [45]. In the present study, FFA conversion is presented in response to variations and interactions of six pairs of independent variable factors when all other variable factors were kept constant.

The relationship between FFA conversion response, the molar ratio of methanol to FFA and the amount of H_2SO_4 (Fig. 2(A)) shows that increasing the molar ratio of methanol to FFA and increasing the amount of H_2SO_4 increased conversion of FFA. The esterification was strongly affected by the amount of H_2SO_4 at lower molar ratios of methanol to FFA. At higher molar ratios of methanol to FFA, however, the amount of H_2SO_4 only slightly affected the reaction. The highest FFA conversion occurred when the molar ratio of methanol to FFA was at center points value (7:1) and the amount of H_2SO_4 was at maximum value (10 wt.%). However, large amount of H_2SO_4 would result in a product of a darker colour and a more difficult purification process [46].

The conversion of FFA significantly increased in response to increments of the amount of H_2SO_4 in the reaction mixture at short reaction times (Fig. 2(B)). However, at reaction times longer than the center point value (70 min), FFA conversion was slightly affected by increments of H_2SO_4 in the range studied. This might indicate that the esterification reaches an equilibrium state, hence further increase of reaction time and H_2SO_4 could only slightly change the conversion of FFA [30].

Fig. 2(C) shows the response surface of FFA conversion as a function of the molar ratio of methanol to FFA and reaction time while other factors were fixed at their center point values. Increasing the value of the molar ratio of methanol to FFA and duration of the reaction to their center point values increased FFA conversion. Further increasing the values of these factors reduced FFA conversion, as indicated by the parabolic shape of the response surface. This reduction would occur because excess methanol in the esterification reaction reduces catalytic activity by diluting the concentration of acid catalysts [47,48].

The surface response plot of FFA conversion as a function of the amounts of H_2SO_4 and MTBE in the reaction (Fig. 2(D)) shows that increasing the amount of MTBE above 17.5 wt.% had a negative effect on FFA conversion when low amounts of H_2SO_4 (< 4.7 wt.%) were present in the reaction. This effect is caused by the dilution of the H_2SO_4 catalyst by the increased amount of MTBE [42,49]. However, at higher amounts of H_2SO_4, increments of MTBE had no significant effect on FFA conversion.

Fig. 2(E) shows that when the molar ratio of methanol to FFA and the amount of MTBE co-solvent are at their center point values, FFA conversion rises above 97.5 wt.% in response. The increased conversion of FFA will occur because MTBE in the reaction system improves the solubility of the oil phase in the methanol, which overcomes the limitation of mass transfer during esterification [21,41,43].

The response surface plot of FFA conversion as a function of reaction time and the amount of MTBE in the reaction (Fig. 2(F)) reveals that increments of MTBE have a negative effect on FFA conversion at reaction times below the center point value of 70 min. This reduction in conversion is due to the dilution effect [20,49]. However, longer reaction times can improve the esterification of FFA and methanol to increase FFA conversion. The effect of the co-solvent on the reaction processes was in agreement with Palipote’s study [42], in which the co-solvent not only had a positive effect by improving the mass transfer limitation but also had a negative effect by diluting the reaction mixture in the process. Therefore, the amount of co-solvent used in the reaction should be carefully considered.

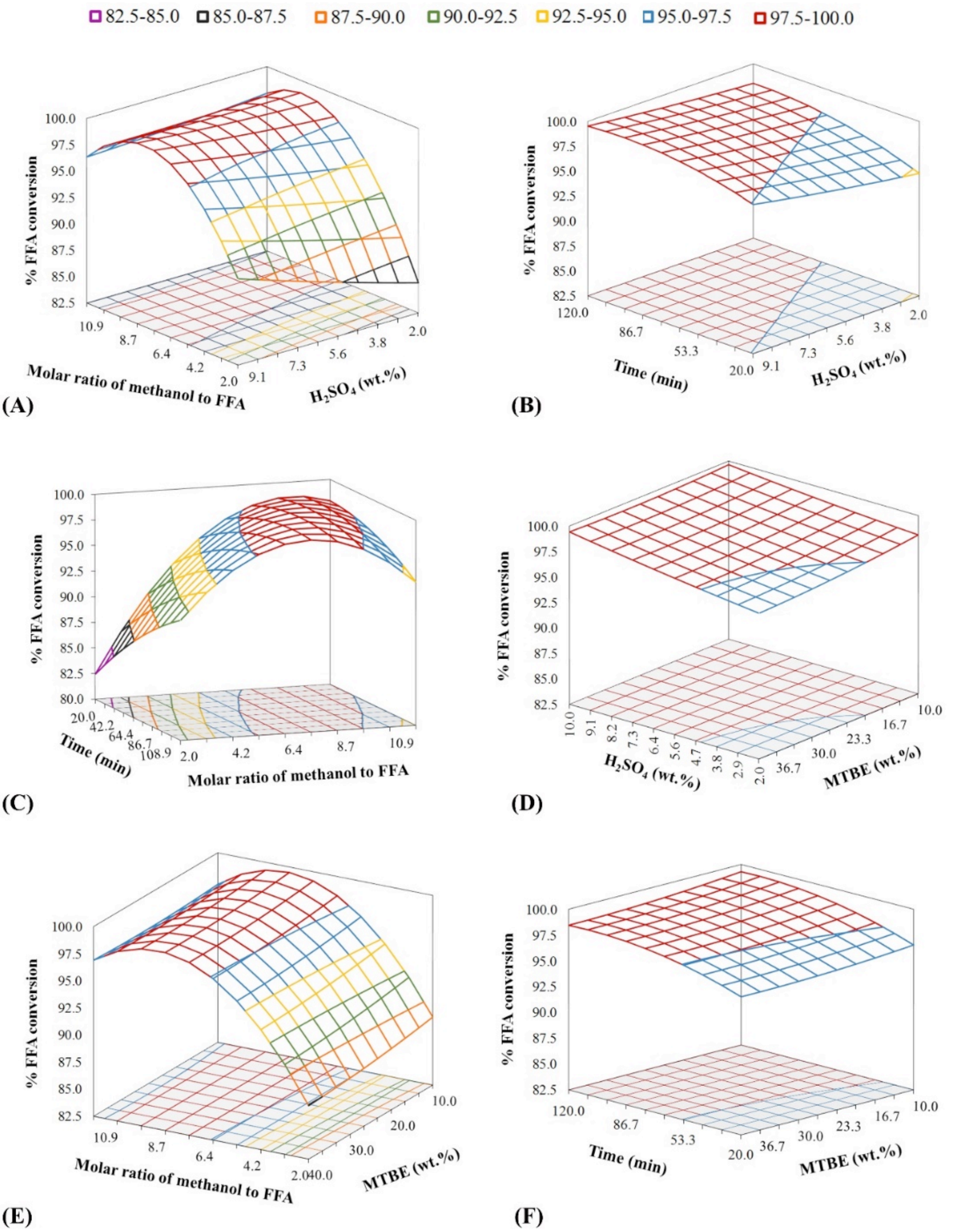

Fig. 2. 3D response surfaces of FFA conversion as functions of six treatments (A) molar ratio of methanol to FFA and amount of H_2SO_4, (B) reaction time and amount of H_2SO_4, (C) reaction time and molar ratio of methanol to FFA, (D) amounts of H_2SO_4 and MTBE, (E) molar ratio of methanol to FFA and amount of MTBE, (F) reaction time and amount of MTBE

3.3. Effect of co-solvent on PFAD esterification

The conditions of esterification as follows: the temperature at 55 °C, the molar ratio of methanol to FFA at 7:1, the amount of H_2SO_4 at 10 wt.% and the reaction time at 70 min were chosen for evaluated the effect of co-solvent addition on the reaction.

In this study, the comparison on the composition of biodiesel produced by 25 wt.% of MBTE co-solvent added in the above conditions with the composition of biodiesel produced by a process without a co-solvent was observed. The effect of MTBE on the composition of the biodiesel after esterification is shown in Fig. 3. The results revealed that esterification was improved by adding 25 wt.% MTBE due to the fact that MTBE increased solubility between FFA and methanol in the reaction. The purity (ester content) of PFAD biodiesel increased from 94.02 to 96.80 wt.% while unreacted FFA decreased from 1.65 wt.% to 0.99 wt.% when MTBE was added to the reaction system. Moreover, residual monoglycerides, diglycerides and triglycerides in the biodiesel decreased from 4.11 wt.% to 2.00 wt.% when MTBE was applied. This means that the MTBE co-solvent also improved the acid-catalyzed transesterification of glycerides with methanol into biodiesel in the side reaction.

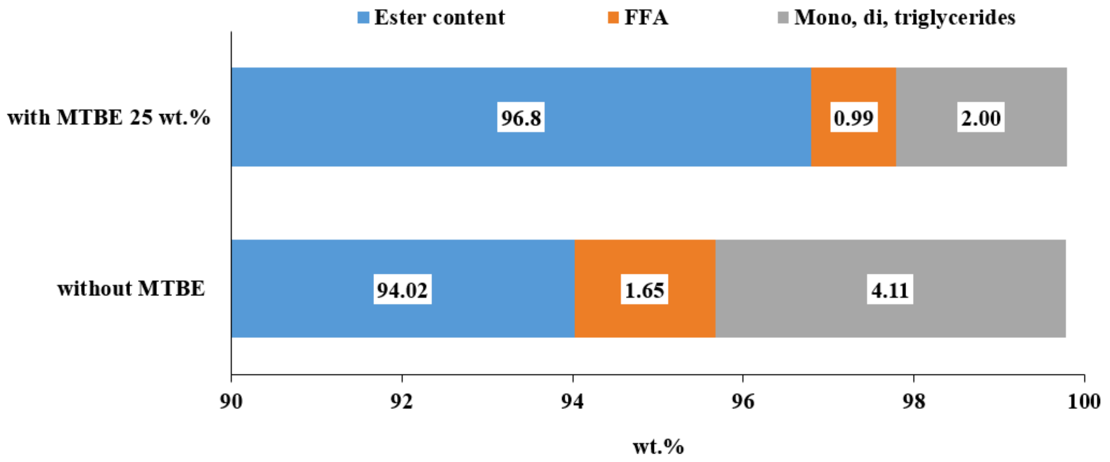

Fig. 3. The Effect of co-solvent addition on biodiesel components after esterification

3.4. Fuel properties

Fuel properties of the PFAD biodiesel obtained in the optimal condition of esterification using a co-solvent are shown in Table 4. The data show that the PFAD biodiesel has a satisfactory purity of 96.80 wt.%. The fuel properties of density, viscosity, sulfated ash, flash point, copper strip corrosion, cetane number and water content, are in compliance with the Thai community-based biodiesel specifications.

Table 4. Fuel properties of PFAD biodiesel

Fuel properties	**Result**	**Community-based biodiesel specification**
Ester content (wt.%)	96.80	-
Residual glycerides (wt.%)	2.00	-
Density (kg/m^3)	870	860-900
Viscosity (cSt)	4.22	1.9-8.0
Sulfated ash (wt.%)	0.001	0.02 max
Flash point (°C)	160	120 min
Copper strip corrosion (no)	no.1	no.3 max
Cetane number	53	47 min
Water content (wt.%)	0.03	0.2 max

4. Conclusion

PFAD is the useful alternative feedstock for biodiesel production by esterification since it consisting of 93 wt.% of FFA. The esterification of PFAD with a co-solvent was successfully optimized using RSM. The RSM approach showed the relationship of each reaction condition that affected the conversion of FFA. The optimal conditions were determined as a molar ratio of methanol to FFA of 7:1, an amount of H_2SO_4 of 10 wt.%, a reaction time of 70 min, and an amount of MTBE of 25 wt.%. These conditions generated an FFA conversion of 98.93 wt.%. The PFAD biodiesel obtained from the MTBE co-solvent system had a higher ester content (96.80 wt.%) and lower contents of unreacted FFA and glycerides (0.99 wt.% and 2.00 wt.%, respectively) than biodiesel produced from a co-solvent-free system. Thus, the MTBE co-solvent successfully improved PFAD biodiesel production by increasing the reaction rate of esterification and acid-catalyzed transesterification to yield a good quality PFAD biodiesel that conformed to the community-based biodiesel specifications.

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