Feasibility of using static mixers for reduction of free fatty acid in mixed crude palm oil via continuous acid-catalyzed esterification

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Abstract

Major problem to produce the biodiesel from mixed crude palm oils (MCPO) is the free fatty acid (FFA) content. To achieve good conversion from MCPO to esters, the FFA should not exceed 1 wt.%. In this study, the reduction of FFA in MCPO with methanol (MeOH) in the presence of H_2SO_4 as an acid catalyst was performed in the static mixers (SM) by a continuous acid-catalyzed esterification. The objective of this study was to determine the possibilities of using SM as a continuous-flow reactor for reducing the FFA in MCPO. Continuous-esterification process was carried out to study the effect of the three important reaction variables (methanol concentration, sulfuric acid concentration, and Reynolds number of MCPO flow rate in the pipeline) to reduce FFA. Results indicated that the FFA of MCPO was reduced from 12.785 wt.% to less than 0.2 wt.% with 20 and 36.8 vol.% of methanol concentration, 0.3 and 2.0 vol.% of sulfuric acid concentration, 3.2 to 36.8 $L.hr^{-1}$ of MCPO flow rate, and mixed more than 0.6 meters in length of SM reactor. In the analysis method, the esterified oil was cleaned three times with water to eliminate the residual acid-catalyst and methanol. The product was analyzed by using a thin layer chromatograph with flame ionization detection (TLC/FID).

Keywords*:* static mixer, reduction, continuous, mixed crude palm oil, esterification

1. Introduction

Biodiesel is a renewable alternative fuel that can be produced from vegetable oil or animal fats, without any engine modification [1]. In Thailand, crude palm oil (CPO) and mixed crude palm oil (MCPO) are used as an alternative feedstock for biodiesel production. However, the major problem for producing biodiesel from CPO or MCPO is the free fatty acid (FFA) content. To achieve good conversion from MCPO to esters, the FFA should not exceed 1 wt.%. [2]. If the FFA level exceeds this amount, it will react with base-catalyst to produce soap as a sponification reaction. As a result, ester conversion was reduced by the formation of soap [3]. In acid-catalyzed esterification, the FFA was converted to esters by direct esterification with acid-catalyst. Esterification reaction was shown in Eq. (1).

$$\underset{\text{FFA}}{\text{RCOOH}} + \underset{\text{Alcohol}}{\text{R}'\text{OH}} \xleftrightarrow{H_2SO_4} \underset{\text{Ester}}{\text{RCOOR}'} + \underset{\text{Water}}{H_2O} \quad (1)$$

where R and R′ denote any hydrocarbon chain.

Currently, many researchers have studied the production and optimization of biodiesel from vegetable oils and alcohols with base or acid catalyzed transesterification in the stirred tanks reactor. However, few researchers have studied the production of biodiesel by static mixers alone. For instance, Thompson and He [4] studied the possibilities of using static mixers as a continuous-flow reactor for biodiesel production from canola oil. Methyl ester was produced under varying conditions and a closed-loop static mixer as a reactor was used. The results showed that the static mixers can be used for biodiesel production. Moreover, the lowest total glycerides can be achieved at the condition: reaction temperature of 60 °C, 1.5 wt.% NaOH (25 wt.% solution in MeOH), and the reaction time of 30 min. Alamsyah et al. [5] studied the comparison of static mixer and blade agitator reactor in biodiesel production from refined palm oil via transesterification with methanol in the presence of potassium hydroxide (KOH) as a catalyst. All experiments were fixed the molar ratio of 1:10.5, 1 wt.% KOH, and varying reaction temperatures of 50, 55, 60, 65, and 70 °C. They reported that the methyl ester content of 96.5 wt.% was achieved with using the SM reactor. Moreover, it can decrease the reaction time more than stirred tank. Therefore, they concluded that the SM reactor has much more effective of mixing than blade agitator.

In an extensive searching, no researcher had yet studied the reduction of high free fatty acid in

oils using the static mixer alone as a reactor under a continuous esterification. Consequently, a key part of this study is the static mixers, also known as motionless mixer, are mixing devices without any moving parts and it was inserted into a housing or pipeline [4]. Static mixers were applied to mix the reaction mixture (MCPO, MeOH, and H_2SO_4) for reducing the FFA in the continuous acid-catalyzed esterification. There are several advantages that static mixers have over continuous stirred tanks reactor (CSTR) such as low capital cost, low operating cost, low maintenance cost, small-space requirements, and short reaction time [6].

2. Materials and methods

2.1 Materials

Mixed crude palm oils (MCPO) containing the FFA of 12.785 wt.%, with a mean 772.1 g/mol molecular weight, 0.916 kg/L density, and 0.01817 Pa.s dynamic viscosity at 60 °C, were used as the feedstock in the continuous acid-catalyzed esterification process. The MCPO was purchased from a small-scale palm oil extracting facility in southern Thailand. All chemicals used in the experiments, which include 99% sulfuric acid (H_2SO_4), and 98% methanol (MeOH), are of commercial grade. A thin layer chromatograph with flame ionization detection (TLC/FID) (IATROSCAN MK-65;, Mishubishi Kagahu Latron Inc.; Tokyo, Japan) was used to analyze the FFA. Analysis used the following chemical standards: tripalmitin, palmitic acid, methyl palmitate (sourced from Nacala Tesque); 1,3-distearin; DL palmitin (mono palmitin) (sourced from Sigma Aldrich); and 1,2-di-stearin 99%, (sourced from Research Plus) were used for the analyses.

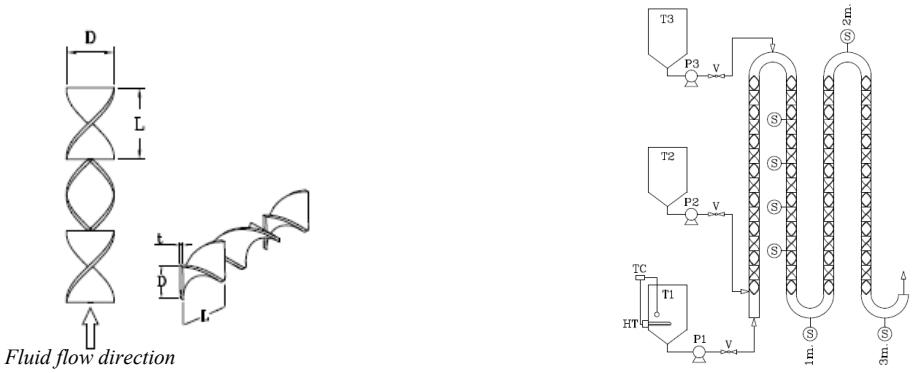
2.2 Methods

2.2.1 Apparatus

Fig. 1 a) is the geometry of static mixer. Each element of static mixer was twisted angle of 180° with the length to diameter ratio (L/D) of 1.5. The adjacent twisted elements were connected to the next element by 90°, as called a twisted-ribbon type. Each mixing element has the dimensions of 10 mm in diameter and 15 mm in length. Fig. 1 b) is a schematic diagram of the experiment setup. The 304 stainless steel of static mixers were inserted into the perfluoroalkoxy (PFA) tube which used as the continuous reactor. PFA tube has the dimensions of 10 mm in ID, 1 mm in thickness, and approximately 4000 mm in length. The MCPO, methanol, and sulfuric acid were continuously fed into the reactor via digital dosing pumps of Grundfos alldos models: DME 48-3, DME 16-6, and DME 2-18, respectively.

2.2.2 Procedures

The MCPO in the tank was preheated to 60°C, in order to reduce its viscosity, by an electric heater that was submerged in the tank. The temperature of the heating oil was controlled at 60°C. Initially, the MCPO, methanol, and sulfuric acid were continuously fed into the SM reactor in the required conditions by digital dosing pumps. In premixed process, MCPO and methanol were mixed through the 1 meter of SM reactor. Subsequently, the sulfuric acid was added into the continuous SM reactor at the H_2SO_4 feeding port after premixed process. Samples were collected at the sampling ports at the position of 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, and 3.0 meters when measuring from the H_2SO_4 feeding port. Each of the samples was quickly cooled, with 0 °C water to stop the reaction, and the compositions of the samples were analyzed using TLC/FID.



(a) (b)

Fig. 1 a) Geometry of static mixer (L: length of element, D: diameter of element, and t: thickness of element). b) Schematic diagram of the experiment setup (S: sampling position, T1: MCPO tank, T2: methanol tank, T3: sulfuric acid tank, P1: MCPO pump, P2: methanol pump, P3: sulfuric acid pump, HT: heater, V: valve, and TC: temperature control)

2.2.3 Theory

In a design of static mixer, Reynolds number is a dimensionless correlating parameter for static mixer design which this parameter is given by Eq. (2), [6].

$$\mathrm{Re} = \frac{\rho V D_H}{\mu} \qquad (2)$$

where ρ is the density of the fluid (kg/m^3), V is the mean fluid velocity (m/s), μ is the dynamic viscosity (Pa.s), D_H is the hydraulic diameter ($4A.P^{-1}$, m), A is the pipe cross-sectional area (m^2), and P is the wetted perimeter of the cross-section (m).

The pressure drop in a static mixer can be defined as the ratio of the pressure drop through the mixers to the pressure drop through the open pipe with similar diameter and length. This parameter is given by Eq. (3), [6]. The standard pressure drop equation for open pipe is given by Eq. (4), [6].

$$\Delta P_{sm} = K_L(\Delta P_{pipe}) \qquad (3)$$

where ΔP_{sm} is the pressure drop in a static mixer per unit pipe length (Pa), K_L is the pressure drop ratio for motionless mixer (K_L of 6.9 for the twisted-ribbon type), and ΔP_{pipe} is the pressure drop in the open pipe (Pa).

$$\Delta P_{pipe} = 4f\frac{L}{D}\rho\frac{V^2}{2} \qquad (4)$$

where ΔP_{pipe} is the pressure drop in the open pipe (Pa), f is the friction factor ($16.\mathrm{Re}^{-1}$, for Reynolds numbers < 2000), L is the length of pipe, D is the diameter of pipe (m), V is the velocity of fluid (m/s), and ρ is the density of the fluid (kg/m^3).

3. Results and Discussions

3.1 Effect of concentration of methanol

The effect of methanol concentration of 3.2, 20, and 36.8 vol.% on the FFA in esterified oil at the conditions: 2 vol.% of sulfuric acid, MCPO flow rate of 20 L.hr^{-1} ($Re \approx 35.7$), and reaction temperature of 60 ^{o}C is shown in Fig.2. The results showed that a tendency of the FFA was reduced from 12.785 wt.% to less than 0.2 wt.% with 20 and 36.8 vol.% MeOH. Moreover, The FFA was rapidly reduced under these 2 concentrations when the mixtures flow through the SM of 0.6 m in length. While, the FFA was slowly reduced between 0 to 1.5 m in length of SM reactor with a methanol concentration of 3.2 vol.%. Noticed that the FFA was steadily reduced to 3.7 wt.% when mixture flow through the SM reactor of more than 2 m in length, but the esterified oil containing the 3.7 wt.% FFA is a too high for producing the biodiesel in a base-catalyzed transesterification.

3.2 Effect of concentration of sulfuric acid

The effect of sulfuric acid concentration of 0.3, 2.0, and 3.7 vol.% on the FFA in esterified oil at the conditions: 20 vol.% of methanol, 20 L.hr^{-1} ($Re \approx 35.7$) MCPO flow rate, and reaction temperature of 60 ^{o}C is shown in Fig.3. The results showed that a tendency of FFA reduction from 12.785 wt.% to less than 0.2 wt.% with 0.3 and 2.0 vol.% H_2SO_4. The FFA was rapidly reduced under these 2 concentrations when the mixtures flow through the SM reactor of 0.6 m in length. Moreover, noticed that the sulfuric acid concentration of 3.7 vol.% has a tendency to reduced slower than the other concentrations. Due to the sulfuric acid has a heavy phase or high density (1.84 g/cm^3) which it is poorly mixed with MCPO and MeOH in the beginning of H_2SO_4 feeding when increasing the H_2SO_4 content. However, the FFA of all concentrations were reduced to less than 0.2 wt.% when the mixture flow through the SM reactor of more than 2 m in length.

3.3 Effect of Reynolds number

The effect of MCPO flow rate of 3.2, 20, and 36.8 L.hr^{-1} in which these oil flow rates can be calculated as of 5.7, 35.7, and 65.6, respectively. Properties of MCPO at 60 ^{o}C are used for calculating the Reynolds number. The effect of Reynolds number on the FFA in esterified oil at the conditions: 20 vol.% of methanol, 2 vol.% of sulfuric acid, and reaction temperature of 60 ^{o}C is shown in Fig.4. The results showed that the FFA can be rapidly reduced from 12.785 wt.% to less than 0.2 wt.% within the SM of 0.6 m in length with every flow rate. Consequently, the Reynolds number does not appear to be a significant process variable because each of conditions has the similar Reynolds numbers. However, a selection of oil flow rate depends on the quantity of esterified oil for biodiesel production in transesterification and the maximum pressure of pump to overcome the pressure drop in the SM reactor. Table.1 shows the pressure drop in a pipeline with and without static mixer.

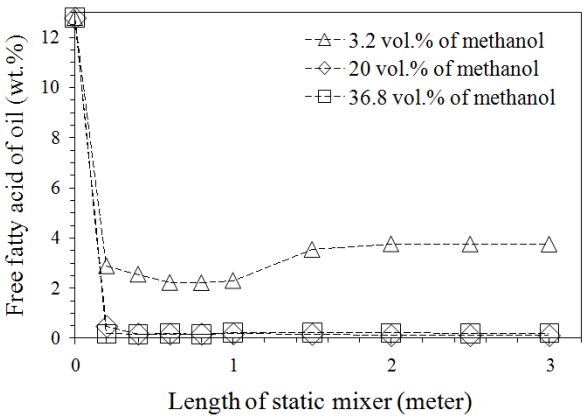


Fig. 2 The effect of methanol concentration on FFA for continuous esterification under following condition: 2 vol.% H_2SO_4, 20 L.hr^{-1} (*Re* ≈ 35.7) MCPO flow rate, and reaction temperature of 60°C

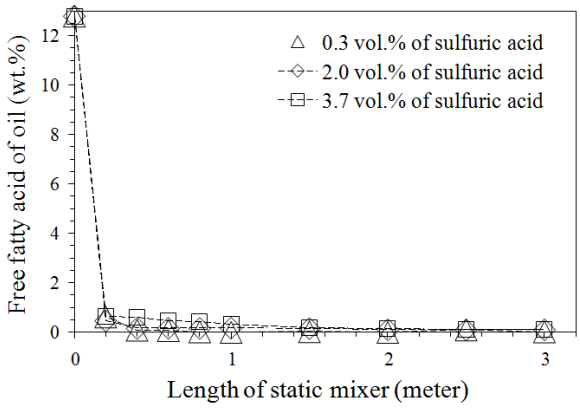


Fig. 3 The effect of sulfuric acid concentration on FFA for continuous esterification under following condition: 20 vol.% MeOH, 20 L.hr^{-1} (*Re* ≈ 35.7) MCPO flow rate, and reaction temperature of 60°C

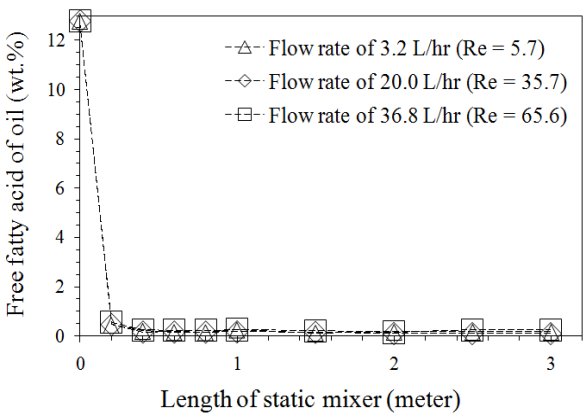


Fig. 4 The effect of MCPO flow rate on FFA for continuous esterification under following condition: 20 vol.% MeOH, 2 vol.% H_2SO_4, and reaction temperature of 60°C

4. Conclusions

The reduction of FFA in MCPO with methanol in the presence of acid-catalyst H_2SO_4 can be achieved in the static mixers by a continuous esterification. Since, the FFA was surprisingly reduced from 12.785 wt.% to less than 0.2 wt.% within 0.6 m in length of SM under 20 and 36.8 vol.% of MeOH, 0.3 and 2.0 vol.% of H_2SO_4, and 3.2 to 36.8 L.hr^{-1} MCPO flow rate. Consequently, the static mixer reactor has a high possibility for reducing the FFA in the continuous-esterification process.

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Table.1 the pressure drop in a pipe with and without static mixer

MCPO flow rate (L.hr^{-1})	Reynolds number in pipeline	Pressure drop (Pa)					
		Length of without SM (m)			Length of with SM (m)		
		1	2	3	1	2	3
3.2	5.7	66	132	198	454	908	1362
20.0	35.7	411	822	1233	2838	5676	8514
36.8	65.6	757	1514	2271	5222	10444	15666

6. References

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