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Optimization of high free fatty acid reduction in mixed crude palm oils using circulation process through static mixer reactor and pilot-scale of two-step process

Krit Somnuk, Suhdee Niseng, Gumpon Prateepchaikul *

Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

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ABSTRACT

High free fatty acid (FFA) reduction in mixed crude palm oil (MCPO) was performed with methanol (MeOH) and sulfuric acid (H_2SO_4) as acid catalyst using the circulation process through static mixer reactor. In this study, the response surface methodology (RSM) was adopted to optimize the acid value in esterified oil after esterification process (first-step) in lab-scale. The results showed that acid value was reduced from 30 mgKOH g^{-1} to 2 mgKOH g^{-1}, when 19.8 vol.% MeOH, 2.0 vol.% H_2SO_4, reaction temperature 60 °C, 40 L h^{-1} of MCPO, 50 min reaction time, and 5-m of static mixer in length, were used in the lab-scale. This recommended condition was used to develop the pilot-scale process in which the scaling up of the FFA reduction from 5 L MCPO of lab-scale to 60 L MCPO of pilot-scale, which was designed on the basis of a simple operation and maintenance. In the pilot-scale process, the lower 1 mgKOH g^{-1} of acid value was achieved when it was conducted at the reaction time of 50 min. In the base-catalyzed transesterification (second-step) of pilot-scale process, the 98.65 wt.% of methyl ester purity was achieved when the following condition: 20 vol.% MeOH, 8 gKOH L^{-1} oil, and 60 min reaction time at 60 °C, was used to produce biodiesel.

1. Introduction

Biodiesel, renewable alternative fuel, can be produced from vegetable oils or animal fats with esterification and transesterification reactions. The high quality biodiesel has demonstrated that it can be used with diesel engines without any engine modification [1,2]. In Thailand, both crude palm oil (CPO) and mixed crude palm oil (MCPO) were mainly used to produce biodiesel. However, the major problem of biodiesel production from MCPO or CPO is the free fatty acid (FFA) content. The FFA must not exceed 2 mgKOH g^{-1} (or 1 wt.%) in order to achieve a good conversion of esters from oil when base-catalyzed transesterification reaction is employed [3–5]. Because, the ester conversion was reduced by the formation of saponification reaction [6,7].

The two-step biodiesel production was used to investigate the purity of methyl ester from the high FFA oils. Esterification reaction (first-step, FFA reduction process), the FFA is converted to esters by the acid-catalyzed esterification. Acid-catalyst (most frequently used: sulfuric, sulfonic, and hydrochloric acids) was used to reduce the FFA in oil [7–9], followed by the base-catalyzed transesterification (second-step, biodiesel production process) to convert the tri-, di-, mono-glyceride to esters. Esterification and transesterification reactions were shown in Eq. (1) [10] and Eq. (2) [5], respectively.

$$\text{FFA} + \text{Alcohol} \overset{\text{Acid-catalyst}}{\leftrightarrow} \text{Ester} + \text{Water} \quad (1)$$

$$\text{Triglycerides} + \text{Alcohol} \overset{\text{Base-catalyst}}{\leftrightarrow} \text{Glycerol} + \text{Esters} \quad (2)$$

Many researchers studied the two-step biodiesel production from high FFA oils with homogeneous acid catalyst and followed by the homogeneous base catalyst by using small scale laboratory equipments (e.g. beaker, flask, glass tube, etc.). For instance, Berchmans and Hirata [11] studied the biodiesel production from crude *Jatropha curcas* L. seed oil (CJCO) having a free fatty acids content of 15% in a 15 mL special reaction glass tube both first- and second-step. They reported that the FFA in CJCO can be reduced to less than 1% with 0.60 w/w of methanol to oil ratio, 1 wt.% of sulfuric acid (H_2SO_4), 60 min of reaction time at 50 °C. In the second step, methyl esters was achieved 90% yield when using 0.24 w/w methanol to oil, 1.4 wt.% sodium hydroxide (NaOH) to oil, and 120 min reaction time at 65 °C. Nakpong and Wootthikanokkhan [12] studied the high free fatty acid coconut oil for producing biodiesel

* Corresponding author.
E-mail address: gumpon.p@psu.ac.th (G. Prateepchaikul).

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Table 1
Physical properties and composition of MCPO and of the product after esterification.

Property	MCPO	Esterified oil	
		Lab-scale (5 L of MCPO)	Pilot-scale (60 L of MCPO)
Density at 60 °C (kg/l)	0.916	0.893	0.889
Viscosity at 60 °C (cP)	18.17	7.60	7.30
Free fatty acid (wt.%)	13.699	0.868	0.457
Tri-glyceride (wt.%)	83.116	80.126	73.261
Di-glyceride (wt.%)	2.882	8.459	8.056
Mono-glyceride (wt.%)	0.244	1.439	1.837
Ester (wt.%)	0.059	9.877	16.389
Water content (%)	0.312	0.117	0.099
Acid value (mgKOH g^{-1})	30.0	1.9	1.0
Methanol content (wt.%)	–	1.410	1.270

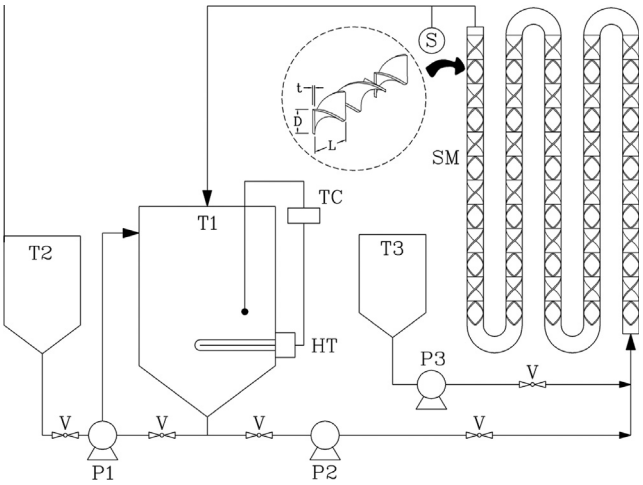

Fig. 1. Schematic diagram of the experiment setup. (T1: MCPO tank, T2: methanol tank, T3: sulfuric acid tank, P1: circulating pump, P2: mixture pump, P3: sulfuric acid pump, HT: heater, V: valve, TC: temperature control, SM: static mixer, S: sampling port, D: diameter of SM, t: thickness of SM, and L: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

using the flat bottom reaction flask and hotplate with magnetic stirrer. In the first step, the FFA in coconut oil was reduced from 12.8% to 0.6% with methanol to oil ratio of 0.35 v/v, H_2SO_4 of 0.7 vol.%, reaction time of 60 min at 60 °C. Subsequently, the esterified oil was transesterified with the following condition: methanol to oil ratio of 0.4 v/v, potassium hydroxide (KOH) of 1.5 wt.% per volume of oil, reaction time of 60 min at 60 °C, with this condition, the 98.4 wt.% of methyl ester can be achieved. Charoenchaitrakool and Thienmethangkoon [13] studied the optimization for biodiesel production from waste frying oil through two-step catalyzed process using the round-bottom flask. They found that the optimal conditions of first step were methanol to oil molar ratio of 6:1:1, 0.68 wt.% H_2SO_4, 60 min reaction time at 51 °C. In the second step, the 90.56% methyl ester content can be produced with 1 wt.% KOH, 9.1:1 methanol to oil molar ratio, 60 min reaction time at 55 °C. Nevertheless, the chemical reactor type of both batch reactor and continuous-flow reactor were mostly used to mix the reactants of mixture in the two-step process, especially, using in the esterification process for reducing the FFA. Therefore, the static mixer reactor was used instead of the stirred tank reactor and small scale laboratory equipments in the FFA reduction process. Moreover, the circulation process of this process has been adopted to replace the agitation process. Static mixer, a mechanical mixer without any moving parts, is often employed in the chemical and food processing industries to mix highly viscous immiscible liquid–liquid phases and to improve the heat and mass transfer of mixture. The common design of static mixer consists of the empty pipe and mixing elements which were inserted into the empty pipe to blend the multi-fluid when fluid flow through static mixer. This mechanical mixer does not have a moving parts, thus, the flow energy is derived from the pressure drop across the length of mixer [14]. Static mixer was typically used in continuous processes for premixing before feeding to a continuous stirred tank reactor (CSTR) but can also be adopted in the closed-loop system to premix before feeding to a batch reactor [15]. There are several advantages of static mixers have over continuous and batch reactors, such as low capital, low maintenance and low operating costs, small-space requirements, and short reaction time [16].

Currently, few researchers have studied the use of static mixer alone in the base-catalyzed transesterification to produce biodiesel from low FFA content in oils. For instance, Thompson and He [17] used the static mixers for expediting the transesterification reaction of canola oil and methanol with NaOH as base-catalyst. They found that the canola methyl ester was produced using a closed-loop static mixer system under varying conditions: reaction temperature of 60 °C, NaOH concentration of 1.5%, and reaction time 30 min. The condition with the lowest total glycerides was 60 °C and 1.5 wt.% catalyst. Alamsyah et al. [18] studied the comparison of static mixer and blade agitator reactor in biodiesel production from refined bleached deodorized palm oil via the transesterification reaction in the circulation process. Comparison between the static mixer and blade agitator in potential mixing process improvement of biodiesel production, the reaction rate in static mixer reactor was faster than blade agitator. The optimal condition for operating with static mixer reactor was 65 °C reaction temperature, reaction time of 5 min, oil to methanol ratio of 1:10.5, and KOH of 1 wt.%. Moreover, very few researchers have studied the acid-catalyzed esterification using static mixer alone to reduce FFA in oils, followed by base-catalyzed transesterification. Somnuk et al. [10] has studied the continuous acid-catalyzed esterification for free fatty acids reduction in mixed crude palm oil using static mixer coupled with high-intensity ultrasonic irradiation. RSM method was employed to optimize the MeOH and H_2SO_4 concentrations. The results showed that the 18 vol.% MeOH, 2.7 vol.% H_2SO_4, and 20 L h^{-1} MCPO were recommended with this condition. The acid value could be reduced from 28 mgKOH g^{-1} to less than 2.30 mgKOH g^{-1} after 2-m in length of static mixer alone.

The above reviews induce the objective of this work to study the optimization of parameters; MeOH concentration, H_2SO_4 concentration, reaction time, length of static mixer, and MCPO flow rate, in the 5 L of lab-scale process for reducing the acid value using

Table 2
Coding of independent variables.

Independent variable	Coded level				
	−1.414	−1	0	+1	+1.414
M: Methanol concentration (vol.%)	5.9	10	20	30	34.1
A: Sulfuric acid concentration (vol.%)	0.6	1	2	3	3.4