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Optimization of continuous acid-catalyzed esterification for free fatty acids reduction in mixed crude palm oil using static mixer coupled with high-intensity ultrasonic irradiation

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ABSTRACT

The major problem of biodiesel production from mixed crude palm oils (MCPOs) is the high free fatty acid (FFA) content. To achieve good conversion from MCPO to esters, the FFA should not exceed 1 wt.% or 2 mgKOH g^{-1} of acid value when using base-catalyzed transesterification to produce biodiesel. In this study, reduction of the acid value in MCPO with methanol in the presence of sulfuric acid as an acid-catalyst was performed in continuous esterification using static mixer coupled with ultrasonic reactor. A 1000 W ultrasonic homogenizer was operated at 18 kHz frequency in a 100 mL continuous-reactor. Response surface methodology (RSM); a 5-level, 2-factor, central composite design (CCD), was employed to optimize the two important reaction variables (methanol and sulfuric acid concentrations). To minimize chemical costs in order to reduce the acid value from 28 mgKOH g^{-1} to less than 2 mgKOH g^{-1}, 18 vol.% of methanol, 2.7 vol.% of sulfuric acid, and 20 L h^{-1} of MCPO flow rate are recommended.

1. Introduction

Biodiesel is a renewable alternative fuel that can be produced from vegetable oils or animal fats, without any engine modification [1]. In Thailand, crude palm oil (CPO) and mixed crude palm oil (MCPO) were used as alternative feedstock for biodiesel production. However, the free fatty acid (FFA) content in MCPO or CPO is a major problem to produce biodiesel. To achieve good conversion from MCPO to esters, the FFA should not exceed 1 wt.% [2]. This corresponds to an acid value (*AV*) of 2 mgKOH g^{-1} when base-catalyzed transesterification reaction is employed. If the acid value level exceeds this amount, it will react with the base to produce soap (saponification process). As a result, ester conversion is decreased by the formation of soap [3,4]. In acid-catalyzed esterification, the FFA is converted to esters by direct esterification with an acid-catalyst Eq. (1) [5].

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

where R and R′ denote any hydrocarbon chains.

To reduce FFA, mixed crude palm oils are normally mixed with a solution of alcohol and acid-catalyst in a stirred tank reactor. This process is time and energy consuming. Using ultrasound instead of a mechanical stirrer, the reaction time can be shortened. Ultrasonic irradiation can generate acoustic cavitations through high intensity acoustic fields in the medium phase until they reach a cavitation phenomenon that creates a bubble collapse. Before the bubbles collapse, the interior of the bubbles may have a pressure as high as 5000 atm that will cause an instant temperature rise to at least 7200 °C, which, in turn, causes rapid changes in the physical and chemical reactions of the reaction mixture. In addition, the ultrasonic field can increase the interface areas between the immiscible fluids, resulting in rapid mixing in the liquids [6,7].

In high FFA oils, biodiesel can be produced with high yield by a two-stage process; a process of acid-catalyzed treatment, followed by a process of base-catalyzed treatment. The reaction time of this method is shorter than using acid-catalyzed transesterification alone in itself. In the first stage, most FFA is converted to esters by acid-catalyzed esterification. Subsequently in the second stage, triglycerides of the esterified oil are converted to esters by base-catalyzed transesterification [8]. Using a laboratory scale reactor to produce methyl ester from high free fatty acid degummed mixed crude palm oil, Prateepchaikul et al. [9] reduced free fatty acid from 8 wt.% to less than 2 wt.%. The optimal condition for producing methyl ester from high free fatty acid mixed crude palm oil is 1 wt.% of sulfuric acid and 8 vol.% of methanol under temperature of 60 °C and reaction time of 90 min for the first-stage, and 2 wt.% of sodium hydroxide and 16 vol.% of methanol for the second-stage, after which 97.5 wt.% purity of methyl ester can be achieved. Currently, few researchers have studied this two-stage process by using ultrasound for accelerating the reaction in batch

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process, particularly in the studying of reduction of high FFA content in oils. For instance, Worapun et al. [10] studied the optimization of biodiesel production from crude palm oil by using ultrasonic irradiation. CPO has a high FFA which is higher than the limit for direct conversion of triglycerides to methyl ester by base-catalyzed transesterification. The CPO was pretreated to reduce the FFA from 6 wt.% to less than 3 wt.% before being subjected to the base-catalyzed transesterification process. The acid-catalyzed esterification process used a 40 kHz ultrasonic frequency with power of 400 W, methanol to oil molar ratio of 6:1, sulfuric acid of 3 wt.% as a catalyst and ultrasonic irradiation time of 30 min at 30 °C. After the acid-catalyzed esterification reaction, the product was allowed to settle for 8 h. The product was then used for the base-catalyzed transesterification process. Deng et al. [11] studied the acid-catalyzed esterification and base-catalyzed transesterification to produce biodiesel from *Jatropha* oil having a high FFA content. All experiments were carried out in a 210 W ultrasonic reactor. Each mixture of *Jatropha* oil, methanol, and catalyst (H_2SO_4 or NaOH) was filled in a 500 mL three-necked flask. The mixture was stirred at 600 rpm and was submerged in a water bath of ultrasonic cleaner under a controlled reaction temperature of 60 °C. In the first process, 1%, 2%, 3%, 4%, 5%, and, 6 vol.% of H_2SO_4; 16%, 24%, 32%, 40%, and 48 vol.% of MeOH, were used to investigate reduction in the acid value. The results showed that after this pretreatment process, the acid value of *Jatropha* oil was reduced from 10.45 to 1.2 mgKOH g^{-1} under 40 vol.% of MeOH, 4 vol.% of H_2SO_4, and the reaction time of 1 h. Subsequently, the esterified oil was used as the raw material in base-catalyzed transesterification process to study the biodiesel yield. The results indicated that a maximum purity of methyl ester yield of 96.4% was obtained when 1.4 wt.% of NaOH, 24 vol.% of methanol, and the reaction time of 30 min were employed. Hayyan et al. [12] studied the reduction of free fatty acids in crude palm oil using ultrasonic energy in the acid-catalyzed esterification process. In the esterification process, acid catalysts (sulfuric acid, methanesulfonic acid, and hydrochloric acid) were used to reduce the FFA content in the CPO. They reported that FFA in the CPO was reduced from 8.7 wt.% to less than 1 wt.% when using 335 W, 47 kHz ultrasonic bath at a combined condition of 2 wt.% of hydrochloric acid, methanol to oil molar ratio of 15:1, and reaction time of 90 min.

To the best of our knowledge, no researchers have yet studied the continuous esterification of high FFA in oils using static mixer (SM) coupled with ultrasound. In the continuous esterification process, the reactants (MCPO, MeOH, and H_2SO_4) were pre-mixed with a static mixer and ultrasound was used to accelerate the reaction. Thus, the key parts of this study are the uses of static mixer and ultrasonic irradiation. Static mixer is also known as 'motionless mixer' or a mixing device without any moving parts. Elements of a static mixer were inserted into a housing or tube [13]. Static mixers had been applied to blend the reaction mixture for reduction of FFA in continuous acid-catalyzed esterification. There are several advantages that static mixers have over continuous stirred tanks, such as low capital, low operating and low maintenance costs, small-space requirements and short reaction time [14].

The above reviews induce the objective of this present work to study the optimization of two key parameters; methanol concentration and sulfuric acid concentration, in continuous acid-catalyzed esterification for the reduction of acid value of MCPO to be less than 2 mgKOH g^{-1} via the use of static mixer coupled with ultrasonic irradiation. Response surface methodology (RSM), a 5-level 2-factor central composite design (CCD), is employed to optimize these two parameters. The main goal is to determine the appropriate response surface models of the relationship between acid values of the esterified oil and these parameters.

2. Materials and methods

2.1. Materials

Mixed crude palm oil (MCPO) having acid value of 28 mgKOH g^{-1}, with a mean 772.1 g/mol molecular weight, 0.916 kg/l density, 18.17 cP viscosity at 60 °C and 12.785 wt.% FFA, was used as feedstock in the acid-catalyzed esterification process. The oil was purchased from a small-scale palm oil extracting facility in southern Thailand. All chemicals used in the experiments, which include the 99% sulfuric acid (H_2SO_4) and the 98% methanol (MeOH), are of commercial grade. Analytical grade potassium hydroxides (KOH), isopropyl alcohol (IPA) and phenolphthalein (pH indicator) are used to determine the acid value of the esterified oil.

2.2. Methods

2.2.1. Apparatus

Fig. 1 is a schematic diagram of the experiment setup. The key parts of continuous acid-catalyzed esterification process are the static mixer and the ultrasonic homogenizer. In the continuous static mixer, each element of the static mixer was twisted 180° with a length to diameter ratio (L/D) of 1.5. Each element was connected to the next element by 90°, the type so called a twisted-ribbon. Each mixing element has dimensions of 10 mm in diameter, 15 mm in length, and 1 mm in thickness.

In the continuous ultrasonic reactor, a 1000 W 18 kHz ultrasonic homogenizer, ACME-KORN, Thailand, model AKHGZ-50420K, was used as the ultrasound source to reduce the acid value of the MCPO. A small cylindrical vessel made with low carbon stainless steel (SUS316L), having dimensions of 34 mm ID, 150 mm height and 8 mm thickness, was used as the ultrasonic reactor. Since acoustic energy density (AED) or volumetric energy density is defined as the ultrasonic power (P_{US}, W) divided by the total volume of the mixture (V_{total}, mL), as expressed in Eq. (2) [15], reaction of the mixture in the 100 mL (net volume after immersion of the horn to be described) ultrasonic reactor was accelerated by an acoustic energy density of 10 W mL^{-1} at maximum ultrasonic power. An ultrasonic horn, manufactured from 316L stainless steel, was tuned to a half-wave acoustic wavelength ($\lambda/2$). The horn, having a length of 135 mm and a horn tip diameter of 28 mm operating at a fixed frequency of 18 kHz, was immersed into the reactant in the reactor until the distance between the horn tip and the bottom of the reactor is not more than 20 mm. Reason is that sulfuric acid, with a relatively high 1.84 kg/l density, will rapidly settle to the bottom of the reactor, and will not mix properly with MCPO if the distance between the horn tip and the bottom of the reactor is larger than 20 mm. Power intensity of the ultrasound was transmitted from the surface of the horn tip to the mixture of the reactant. Ultrasonic irradiation time was controlled by a digital timer installed in the ultrasonic generator. A DC cooling fan was positioned on top of the ultrasonic homogenizer to cool the piezoelectric transducer.

$$\mathrm{AED} = \frac{P_{US}}{V_{total}} \tag{2}$$

2.2.2. Procedures

MCPO in the tank was preheated to 60 °C, in order to reduce its viscosity, by an electric heater submerged in the tank. Temperature of the heated oil was regulated by a temperature control. Generally, MCPO (20 L h^{-1}), MeOH and H_2SO_4 were continuously fed into the 3-m long tube that houses the static mixer and through the 100 mL ultrasonic reactor at predetermined required ratios by