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Effects of mixing technologies on continuous methyl ester production: Comparison of using plug flow, static mixer, and ultrasound clamp

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ABSTRACT

Four types of continuous reactors, namely plug flow reactor (PF), static mixer reactor (SM), ultrasound clamp on tubular reactor (US), and static mixer combined with ultrasound (SM/US) were compared for their purities of methyl ester in biodiesel production from refined palm oil (RPO). The reactor conditions were: KOH 4, 6, 8, 10, and 12 g L^{-1}, methanol content 20 vol.%, and under 20 L h^{-1} RPO flow rate at 60 °C temperature. The highest purity of methyl esters: 81.99 wt.% for PF, 95.70 wt.% for SM, 98.98 wt.% for US, and 97.67 wt.% for SM/US, were achieved with 900 mm, 900 mm, 700 mm, and 900 mm reactor lengths respectively, and 12 g L^{-1} of KOH was used in all cases. The 16 × 400 W ultrasound clamp was operated at 20 kHz frequency, and among short length reactors the US case was more effective than PF, SM, or SM/US. Moreover, ester purity from the US reactor was slightly decreased by the lowest 4 g L^{-1} KOH. The US reactor was clearly superior over the other types of continuous reactor, and had the potential to reduce KOH consumption by sonochemical effects on the base-catalyzed transesterification reaction.

1. Introduction

Biodiesel as renewable energy source can be used in diesel engines without any major modification [1,2]. Moreover, the exhaust emissions from biodiesel have advantages over those from petroleum diesel, such as less smoke and airborne particles [3]. Biodiesel is preferable to petroleum diesel in terms of biodegradability and non-toxicity [4,5]. Moreover, biodiesel has lower CO_2 emissions and sulfuric content than petroleum fuel [6]. In the biodiesel production process, various mixing technologies increase the contact of two immiscible phases: oils and alcohol. These include using an agitator, a static mixer, a continuous stirred tank reactor (CSTR), a high shear mixer, or an ultrasonic reactor, and the choice should be made to decrease catalyst concentration, methanol content, operating costs, and maintenance costs, as well as reaction (processing) time [7]. Regarding continuous biodiesel production with static mixer in the reactor, Sungwornpatansakul et al. [8] reported on the potential of mixing to influence completed transesterification. They reported that a droplet of methanol was rapidly mixed with the oils at the beginning of the static mixer. Somnuk et al. [7] optimized a two-stage continuous process to produce methyl ester from mixed crude palm oil (MCPO), using a static mixer coupled with high-intensity ultrasound. In the static mixer, the methyl ester concentrations 92.09 wt.% and 93.03 wt.% were detected at 1 m and 2 m length-wise locations along the static mixer at the optimal operating conditions: 18 vol.% of methanol, 8 g L^{-1} of KOH, 30 °C of temperature, and 20 L h^{-1} of esterified oil. Likozar et al. [9] studied the modeling of chemical equilibrium, reaction kinetics and mass transfer for continuous biodiesel production from canola oil using a tubular reactor combined with static mixer while varying the operating parameters: temperature, volumetric flow rate, phase fractions, and catalyst content. Their models can be used to apply for scale-up from 5 to 10 mm internal diameter of a tubular reactor, using the kinetic parameters in a reaction scheme of individual TG, DG, MG, glycerol and other components of the oil determined using a six flat-blade disk turbine in a batch process [10].

As application of ultrasound in the circulation and continuous biodiesel production process, Choedkiatsakul et al. [11] studied the production of biodiesel from palm oil using a combined mechanical stirrer and ultrasonic reactor. Three reactor configurations were tested: mechanical stirrer with horizontal stirring rod inside the reactor (MS reactor), ultrasound irradiation (US reactor), and combined mechanical stirring and ultrasound irradiation (MS–US reactor) on producing methyl ester. A dual frequency (20 and 50 kHz) ultrasound rectangular reactor of stainless steel (SUS316) was integrated with a horizontal mechanical stirrer to produce biodiesel. High methyl ester yield was achieved by using re-circulation with 5 min reaction time, 6:1 methanol to oil molar

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ratio, and 1% NaOH catalyst loading at 55 mL min^{-1} flow rate on using the MS–US reactor. They found that the number of transducers influenced the ester yield more significantly than the dual ultrasonic frequency (20 or 50 kHz). The combined MS–US reactor had improved biodiesel production over the MS and US reactors. The mechanical stirrer assisted the sonochemistry of transesterification reaction. Therefore, a static mixer will be applied to accelerate the transesterification reaction, combined with sonication by ultrasonic clamps on the tube, for continuous biodiesel production in this current study. Yin et al. [12] studied biodiesel production from soybean oil deodorizer distillate (SODD) using countercurrent pulsed ultrasound. The results showed that the countercurrent pulsed ultrasound emitter (CCPUE) was more effective than the static probe ultrasound emitter (SPUE). With the CCPUE, 96.1% biodiesel conversion was obtained under the optimal conditions: 25 °C temperature, 10:1 M ratio of methanol to triglyceride, 200 mL min^{-1} flow rate, 1.8% catalyst, and 4 s on-time, 2 s off-time cycle of pulsed ultrasound at 50 min total reaction time. Mostafaei et al. [13] optimized continuous biodiesel production from waste cooking oil with response surface methodology using a central composite experimental design. The results showed that 91.12% yield and 102.4 W energy consumption were achieved under the optimal conditions: 75 mm irradiation distance, 28 mm probe diameter, 56% ultrasonic amplitude, 62% vibration pulse, and 50 mL min^{-1} reactant flow rate. Delavari et al. [5] studied ultrasound combined with helicoidal reactor in producing biodiesel by continuous transesterification. The system consisted of a 1500 W ultrasonic homogenizer and glass helicoidal reactor with 20 m tube length. This set-up was submerged in a hot water bath. The optimal conditions were: 8.6 oil to methanol ratio and 0.5 wt.% NaOH at 1 L min^{-1} flow rate of waste cooking oil, and 90% yield was achieved within 150 s in the continuous process. This system was more efficient than conventional batch systems using magnetic stirrer, apparently due to sonochemistry effects of cavitation. In sonochemistry ultrasonic acoustic waves affect chemistry with coupled physical and mass transfer effects, with strong effects stemming from collapsing cavitation bubbles [14]. The contact surface area of chemical reactants and oil can be increased by sonication [15]. Moreover, Martinez-Guerra and Gude (2015) reported that direct ultrasound is significantly more effective than indirect ultrasound [16,17]. As an example of indirect ultrasound, the acoustic wave from an ultrasonic transducer at the wall of an ultrasonic water bath has to travel through water in the bath and through an immersed reactor until before it reaches the reaction mixture. The above literature review of continuous biodiesel production shows that many types of reactor (plug flow, static mixer, and ultrasonic) have been studied to decrease reaction time, chemical costs, operating costs, and maintenance costs. Most studies have examined effects of alternative mixing technologies on ester conversion to produce biodiesel from various oils. However, this current study compares the effectiveness of the purities of methyl esters with short reaction times between these four continuous reactor types: plug flow reactor (PF), static mixer reactor (SM), ultrasound clamp on tubular reactor (US), and static mixer combined with ultrasound (SM/US).

2. Materials and methods

2.1. Materials

Commercial refined palm oil (RPO) was used as the raw material in continuous base-catalyzed transesterification. The composition of RPO was 0.27 wt.% free fatty acid (FFA), 97.10 wt.% triglyceride (TG), 2.29 wt.% diglyceride (DG), 0.35 wt.% monoglyceride (MG), with 783.4 g mol^{-1} mean molecular weight, 883 kg m^{-3} density at 60 °C, and 0.0184 Pa s viscosity at 60 °C as reported in Table 1. For determining the molecular weight of RPO, gas chromatography was used to analyze the fatty acid composition of RPO (see Table 3) reported in percentages by weight (wt.%). The composition was used to calculate the mean molecular weight of RPO. The commercial grade chemical reactants 95% potassium hydroxide (KOH) and 99% methanol (MeOH) were used in the experiments. The analytical grade chemicals were hexane, diethyl ether, formic acid, and benzene. To analyze the biodiesel composition a thin layer chromatography with flame ionization detection (TLC/FID, model: IATROSCAN MK-65; Mishubishi Kagahu Latron Inc., Tokyo, Japan) was used, and the weight percentages of methyl ester, TG, DG, MG, and FFA in the biodiesel and in the RPO were determined. To calibrate the TLC/FID instrument, six standard samples: Tripalmitin, Palmitic acid and Methyl Palmitate (obtained from Nacala Tesque, Inc,, Kyoto, Japan,); 1,3, - Distearin, DL, Palmitin (mono palmitin) (obtained from Sigma Aldrich Co, USA) and 1,2- Distearin 99%, (from Research Plus, Inc, USA) were used as standards to calibrate the peaks of the tri-, di-, and monoglycerides, free fatty acid, and ester.

2.2. Equipment

Fig. 1 shows a schematic of the experimental setup. The continuous reactors for methyl ester production from RPO were of four types: plug flow reactor (PF), static mixer reactor (SM), ultrasound clamp on tubular reactor (US), and the static mixer combined with ultrasound (SM/US). The PF reactor simply consisted of a tube, and it was operated without ultrasound or any mixing elements in the tube. The tube of stainless steel (SUS304) had 13 mm inside diameter, 3.5 mm wall thickness, and 1000 mm length. The Reynolds number (*Re*) was calculated to determine the flow pattern of RPO in the tube. It is defined by Eq. (1). The mixing element of the SM is the key to blending RPO with potassium methoxide, and the mixing elements were inserted into the empty tube. Each static mixing element had 180° twist with length to diameter ratio (L/D) 1.5. The consecutive mixing elements were 90° off at contact, known as twisted-ribbon configuration [18]. The US reactor had the ultrasound clamp on the tubular without SM, and details of the ultrasound clamp are described in the section. Finally, the SM/US reactor had the static mixer combined with ultrasound (SM/US). Table 2 summarizes how the various components were combined in the four continuous reactors.

$$Re = \frac{\rho V D}{\mu} \tag{1}$$

where *Re* is Reynolds number, ρ is the density of the fluid (kg m^{-3}), *V* is the mean fluid velocity (m s^{-1}), μ is the dynamic viscosity (Pa s), and *D* is diameter of the tube (m).

Table 1
Physical properties of RPO.

Property	RPO	Analysis method
Mean molecular weight (g mol^{-1})	783.4	Calculated[a]
Density at 60 °C (kg m^{-3})	883	ASTM D 1298
Viscosity at 60 °C (Pa s)	0.0184	ASTM D 445
Triglyceride (wt.%)	97.10	TLC/FID
Diglyceride (wt.%)	2.29	TLC/FID
Monoglyceride (wt.%)	0.35	TLC/FID
Free fatty acid (wt.%)	0.27	TLC/FID

[a] The mean molecular weight was calculated from the fatty acid composition of RPO, which was analyzed by gas chromatography.