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Enhancement of biodiesel production reaction employing the static mixing

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ABSTRACT

Many reactors or mixers have been developed to enhance the reaction rate and reduce these requirements. In this research, a comparison of two mixing technologies, conventional mechanical mixer and the static mixer, was carried out. The conversion efficiency and kinetics show that the static mixer has a better performance. The static mixer has the potential to deliver better rigorous mixing between the raw oil and methanol, to the point that it can make the dispersed droplets of methanol in the raw oil smaller and more uniform, which resulted in enhancement of the reaction with the possibility of shortening the reaction time associated with biodiesel production.

1. Introduction

Biodiesel is known as one of the alternative fuels, which can be obtained from great variety of renewable feedstock such as pure vegetable oils, waste cooking oils, or animal fats [1,2]. There are many processes for biodiesel production, with the main objective of reducing the viscosity of the raw oil which is one of the major obstacles for long-term utilization of vegetable oil in diesel engines [3]. Transesterification is the most investigated method and has been paid attention by scientists for a long time since 1853 [2–6]. The transesterification reaction is the reaction between triglycerides (TG), which is the main component in the vegetable oil, and alcohol compound. The main product is a mixture of Fatty Acid Methyl Ester (FAME) of long-chain fatty acids such as palmitic, stearic, or oleic acids. There are several variables that have effects on the product yield in transesterification reaction. They are molar ratio of alcohol to raw oil, reaction temperature, type and concentration of catalyst, mixing mechanism, and the raw oil itself [7].

There are many challenges that need to be overcome in biodiesel production by this transesterification process. The basic challenges are that mass transfer is limited because oils and alcohol are immiscible due to the low solubility of short-chain alcohols [8] and the limitation of the conventional mechanical mixing [9–12] and transesterification is known to be a reversible reaction so there is a possibility of the backward reaction which results in product reduction [3].

The intensity of mixing has a strong influence on reaction rate which has been investigated and reported in many studies [13–20]. Many technologies of mixer in reactors have been developed for reaction rate enhancement, such as static mixers which are utilized in this study [19,21]. The main advantage of static mixers is that as the motionless mixers, they typically have lower energy consumptions and reduced maintenance requirements because there are no moving parts. Static mixer consists of a series of fixed geometric mixing elements enclosed within a tubular pipe. The energy of the flow stream itself is utilized to create mixing. The static mixer performs a series of mechanisms to mix reactants, namely dividing, rotating, channeling, or diverting the flow before recombining it [12]. They are very effective in mixing liquids that are not readily miscible under normal conditions. Many researches also showed that static mixer has effective results when applied to transesterification process for biodiesel reaction [22–24] with the possibility for developing into a stand-alone system [22] such as plug flow continuous reactors [25]. In this research, the main goal is to study the kinetics of transesterification process by comparing the reaction kinetics for both static mixing and mechanical mixing methods since most of the studies are focusing on the performance results for both methods but not on the kinetics.

For kinetics studies, there are 3 operating stages in the reaction: first is the slow initial mass transfer stage then the fast chemical controlled stage, and the final slow equilibrium stage [17,20,26]. In many studies, the first mass transfer stage is known to be negligible when the agitation intensity is high enough. The agitation is more significant during the initial slow mass transfer stage than after triggering the reaction. In the second stage, the agitation is not so necessary since the reaction rate could not be enhanced by further agitation [14,17].

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We are focusing on the chemical kinetics by comparing the product yield and droplet sizes of alcohol in the raw oil for both mechanical and static mixings. The transesterification reaction is done under the room temperature since the reaction kinetics will be slow and become more apparent while most of the previous researches are mainly focusing on the production by conventional mechanical mixer under heated temperature [13,15,20]. Some of the work also studied the kinetics of the static mixers [12] but with different methods and calculations. In this research, we changed the molar ratio of methanol to oil and the catalyst concentration instead of changing the temperature.

2. Materials and methods

2.1. Materials

Raw oil utilized in this research is 100% corn oil purchased from the local market with the composition as described in Table 1. Methanol is utilized for reacting with raw oil and potassium hydroxide (KOH) is used as a catalyst in this transesterification reaction.

2.2. Experiment methods

Usually two sets of propeller are required for proper turbulence mixing. In this experiment, the catalyst KOH was mixed with methanol before adding to raw oil. Instead of using a propeller, the mixed solution was stirred with a magnetic stirrer with a bar size of 2 cm, at a speed of 600 rpm for 30 min as shown in Fig. 1.

A water bath stirrer WBS-80A from As One Corporation, Japan, was utilized for both heating and stirring purpose, with a maximum capacity of 3 L for the water tub with a rotation speed range at 100–1200 rpm. The reaction apparatus are shown in Fig. 1.

For another method of mixing, a helical type static mixer (HT), as shown in Fig. 2, is utilized. The length of the pipe is 26 cm, with 0.8 cm internal diameter. The static mixer installed inside consisted of 20 elements and each element had 1.2 cm length and 0.8 cm width with a 1 cm gap between the elements and the pipe exit at both end of the pipe. The components are mixed through the static mixer in 2–3 s with a maximum volumetric flow rate of 0.12 L/s, and a superficial velocity at 0.24 mm/s. After this the product yield had been monitored for 30 min.

2.3. Reaction conditions

In this research, experiments were conducted at the room temperature by changing the molar ratio of methanol to oil and the catalyst concentration only. The temperature is controlled to be at room temperature between 26 and 30 °C. Methanol mole ratio was fixed at 4.3:1 and 6:1, since the mole ratio of 6:1 is the optimum value for transesterification reaction. The mole ratio of 4.3:1 was chosen to prove that even at lower amount of methanol than the optimum value, static mixer is still able to archive high conversion rate. For the concentration of catalyst KOH, the concentration was ranged between 0.6, 1.2, and 1.8% concentration by weight.

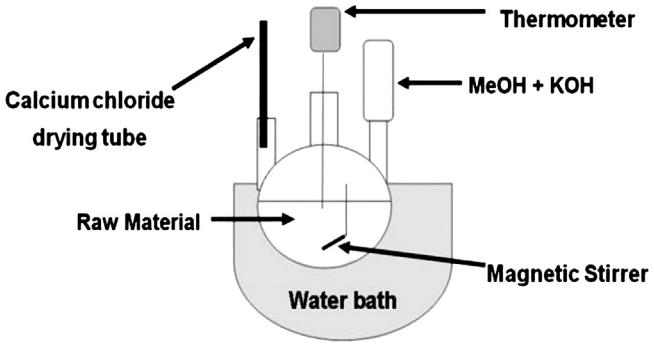

Fig. 1. Mechanical stirring apparatus.

3. Calculation and analysis

3.1. Product analysis

The reaction was analyzed during 30 min of reaction mentioned in above experiment methods. This is the typical operation time for conventional biodiesel production. Samples are taken at 0, 0.5, 1, 1.5, 2, 3, 4, 5, 7, 10, 15, 20, 25, and 30 min respectively. The starting time of the reaction is different for both mixing methods. For the mechanical stirring, the time was counted after all methanol–KOH solution was added to raw oil while the stirrer kept rotating. On the contrary, the starting time of the static mixing method was counted at the outlet of the mixer when the mixed/emulsified product came out. This is because the mechanism of the static mixer showed difficulties in how to locate the beginning of the reaction. Even though the starting time of these two methods was different, the errors of the results are not significant.

After samples were taken, hydrochloric acid was quickly mixed with samples to stop the reaction. Then they were centrifuged to separate the upper FAME layer and only the components in this layer were analyzed. Products are analyzed by GC-2010 of Shimadzu Corporation with the flame ionization detector, following the EN 14103 standard. The capillary column is the ultra-alloy column with a length of 15 m, an internal diameter of 0.25 mm, and a film thickness of 0.1 μm. Helium is utilized as a carrier gas at 2 mL/min flow rate. The injector temperature was 250 °C and the oven temperature was 200 °C. Methyl heptadecanoate was used as the internal standard.

3.2. Droplet size measurement

The droplet sizes of products during 30 min of the reaction were measured by a digital microscope from the time zero to the time of

Table 1
Fatty acid composition in corn oil.

Fatty acids		g per 100 g total fatty acids
Saturated	C16:0 (Palmitic)	11.3
	C18:0 (Stearic)	2.0
	C20:0 (Arachidic)	0.4
	C22:0 (Behenic)	0.1
	C24:0 (Lignoceric)	0.2
Monounsaturated	C16:1 (Palmitoleic)	0.1
	C18:1 (Oleic)	29.8
	C20:1 (Eicosenoic)	0.3
Polyunsaturated	C18:2 n−6 (Linoleic)	54.9
	C18:3 n−3 (α-Linolenic)	0.8

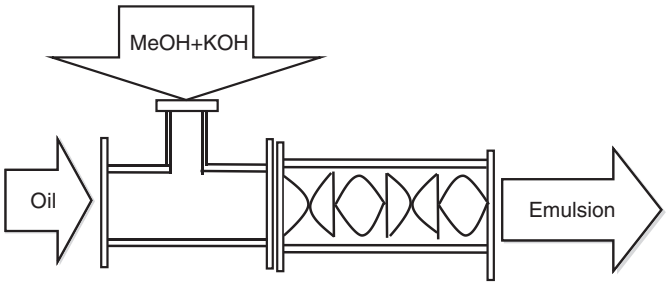

Fig. 2. Static mixing apparatus.