Transesterification of sunflower oil in a countercurrent trickle-bed reactor packed with a CaO catalyst

Sung Mo Son, Katsuki Kusakabe*

Department of Living Environmental Science, Fukuoka Women's University, 1-1-1 Kasumigaoka, Higashi-ku, Fukuoka 813-8529, Japan

ABSTRACT

Transesterification of sunflower oil with methanol to form biodiesel was performed in a countercurrent trickle-bed reactor, using calcium oxide particles 1–2 mm in diameter as a packed, solid base catalyst. Although biodiesel production generally requires a reaction temperature below the boiling point of methanol to maintain a heterogeneous, liquid–liquid reaction, in the present study the reaction temperature was varied from 80 to 140 °C to confirm the progress of transesterification in a gas–liquid–solid phase reaction system. Oil droplets released from a thin tube flowed downward, while vaporized methanol flowed upward in the bed. The effects of the reaction temperature, methanol and oil flow rates, and the bed height on the FAME yield were investigated. The oil residence time in the reactor, which was controlled by changing both the oil flow rate and the bed height, had a significant effect on the FAME yield. In addition, the FAME yield increased with reaction temperature and was maximal at 373 K due to the change in residence time associated with reduced oil viscosity at higher temperatures. The FAME yield was 98% at a reaction temperature of 373 K when the methanol and oil flow rates were 3.8 and 4.1 mL/h, respectively.

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1. Introduction

Biodiesel fuel (BDF) that is made from vegetable oils and animal fats, is a renewable, non-toxic and biodegradable alternative to petroleum diesel fuel. BDF burns cleanly, thus reducing release of greenhouse gases. However, the cost of BDF production remains higher than that of petroleum diesel fuel due to the feedstock and capital costs [1].

The most common method of BDF production is transesterification of triglycerides with methanol in the presence of a homogeneous base catalyst to yield fatty acid methyl esters (FAMEs) and glycerol. Homogeneous base catalysts have been used because they result in adequate reaction rates and product yields. The reaction also proceeds at temperatures lower than the boiling point of methanol and at normal pressure, thereby reducing the capital and operating costs associated with BDF production. However, homogeneous base catalysts have disadvantages such as equipment corrosion and the need to remove residual inorganic components from the BDF waste-water [2]. Furthermore, in the presence of free fatty acids (FFA), alkali-hydroxides lead to soap formation, which reduces the FAME yield. A consequence of these problems is increased BDF production costs [3–6].

A continuous process is preferred for mass production of BDF, since it is more convenient and economical. Transesterification of triglycerides has been investigated for use in continuous reactors, such as a plug flow reactor [7], reactive distillation column [8,9], a combined PFR/CSTR arrangement [10] and a microtube reactor [11,12].

Behzadi and Farid [13] investigated a continuous gas–liquid reactor for BDF production from fats and oils using either sodium methoxide or sodium hydroxide. Heated oils and fats were sprayed into a reaction chamber with countercurrent methanol vapor flow. This process creates a large contact area between the oil and the methanol phase due to the formation of micro-sized droplets, as well as continuous separation of products and unreacted methanol in the reactor. Atsya et al. [14] examined a continuous-flow, liquid–liquid, packed-bed reactor for transesterification of canola oil with a sulfuric acid catalyst. Use of the smallest packed particles and the highest pressure gradient resulted in a reaction rate constant in the packed bed reactor that was similar to that of an open column. This result indicates that the use of a liquid–liquid, packed-bed reactor can effectively overcome the mass-transfer limitations of a heterogeneous two-phase system.

Transesterification of oil with methanol in the presence of heterogeneous catalysts constitutes a liquid–liquid–solid reaction system [15]. The reaction rate of transesterification using a heterogeneous catalyst is lowered by the diffusion resistances at either the liquid–liquid interface or the liquid–solid interface, as compared with that of a homogeneous catalyst [16]. Thus, higher reaction

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* Corresponding author.
  E-mail address: kusakabe@fwu.ac.jp (K. Kusakabe).

Table 1
Basic characteristics of fresh and recycled (4 times) catalyst.

	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Fresh catalyst	4.26	0.0085	8.2
Recycled catalyst (4 times)	4.30	0.0180	19.2

temperatures are required to enhance the reaction rate in the presence of a heterogeneous catalyst. Son and Kusakabe [17] investigated transesterification of sunflower oil (SFO) and waste cooking oil (WCO) with methanol using a CaO catalyst at 80–120 °C under reflux. At a reaction temperature of 80 °C with a 3 wt% CaO catalyst, the FAME yield of SFO and WCO exceeded 92 and 84%, respectively, after 120 min. In addition, the CaO catalyst retained its catalytic activity at elevated temperatures.

Trickle-bed reactors are widely used in heterogeneous gas–liquid chemical processes due to their flexibility and simple operation [15,18]. In the present study, transesterification of SFO with methanol was carried out at a reaction temperature higher than the boiling point of methanol in a bed of packed CaO particles; therefore, a gas–liquid countercurrent trickle-bed reaction system was formed. The effects of the methanol and oil flow rates, the packed bed height, and the reaction temperature on the FAME yield in a trickle-bed reactor were investigated.

2. Experimental

Commercially available calcium oxide (CaO) desiccant and cooking sunflower oil (SFO) were used in the present study. The diameter of the CaO particles was in the range of 1–2 mm or 2–3 mm. The basic characteristics of fresh catalyst and catalyst that had been recycled 4 are seen in Table 1. Dehydrate methanol was obtained from Wako Pure Chemical Ind. Ltd., Japan. The acid and saponification values of the oil were determined using standard titration methods [19]. The molecular weight of the oil was determined from the acid and saponification values. The water content in the oil was determined using a Karl–Fisher moisture titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.).

Fig. 1 shows the experimental apparatus used for BDF production. Transesterification of SFO with methanol was performed in a trickle-bed reactor (inner diameter = 16 mm, length = 200 mm) using packed CaO particles as the catalyst. Methanol and SFO were fed into the reactor with syringe pumps. Methanol was completely vaporized in the heated section at the bottom of the trickle bed and its vapor passed through the CaO catalyst bed. The vapor of unreacted methanol was recovered using a condenser. The SFO was fed through a single tube and was dispersed on the catalyst bed. Unreacted SFO, FAME and glycerol were recovered in the product reservoir. The SFO flow rates tested were 4.1 and 7.7 mL/h. A varied methanol flow rate ranged from 1 to 4 mL/h. CaO particles were packed into the bottom of the reactor and glass beads of the same diameter were loaded into the remainder of the reactor. The amount of packed CaO particles was 7.4, 14.8 and 18.5 g, which were equivalent to bed heights of 5, 10 and 12.5 cm, respectively. The trickle-bed reactor was heated with an electric heater. The reaction temperature was varied from 80 to 140 °C. The reaction product was centrifuged at 6000 rpm for 20 min. The upper ester layer was rinsed with deionized water, and the mixture was centrifuged again. These procedures were repeated several times until the pH value of the aqueous phase reached 7.0. Then 0.1 ml of the rinsed sample was diluted with 3 ml of hexane for analysis.

The concentration of unreacted oil that remained in the BDF products was determined using a high-performance liquid chromatograph (HPLC, Tosoh Corp., Japan) equipped with both a silica-gel column (Shimpack CLC-SIL, Shimadzu Corp., Japan) and
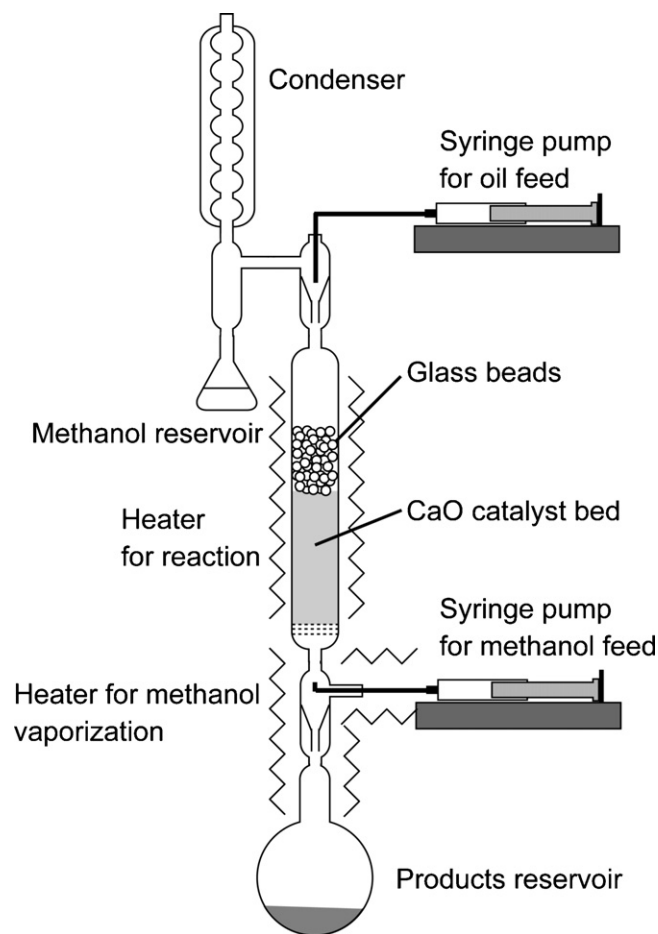

Fig. 1. Tricke bed reactor for biodiesel production.

a refractive index detector. The mobile phase was n-hexane/2-propanol = 99.5/0.5 (v/v) and the column temperature was kept constant at 40 °C. Two peaks that were attributed to the sum of FAMEs and the unreacted glycerides (sum of mono-, di- and triglycerides), respectively, appeared in the liquid chromatogram. The FAME yield in the product was calculated as follows:

$$\text{FAME yield} = \frac{C_{FAME}}{3C_{oil}} \times 100 \qquad (1)$$

where C_{oil} and C_{FAME} are the triglyceride concentration in the reactant and the FAME concentration in the product, respectively [10,11,15].

3. Results and discussion

The acid and saponification values of the SFO were 0.41 mg-KOH/g and 192.4 mg-KOH/g, respectively. The molecular weight of the SFO determined from the acid and saponification values was 877. The predominant fatty acids in the SFO were linoleic acid (56%), oleic acid (37%) and palmitic acid (6%).

BDF production was carried out at a reaction temperature higher than the boiling point of methanol in a packed bed of CaO particles. Therefore, transesterification of triglycerides occurred in a gas–liquid countercurrent trickle-bed reactor. Vaporized methanol became a continuous phase, and the oil droplets were dispersed within the packed bed of CaO. Accordingly, the FAME yield increased linearly with bed height, as shown in Fig. 2, due to an increased residence time in the liquid phase.

Fig. 3 shows the effect of the liquid flow rate on the FAME yield. When the liquid flow rate was greater than 7.1 mL/h, flooding