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In-depth study of continuous production of biodiesel using supercritical 1-butanol

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ABSTRACT

The continuous production of biodiesel from canola oil in supercritical 1-butanol (SCB) was thoroughly examined in order to investigate the detailed reaction behavior and elucidate the reaction kinetics. A continuous reactor was employed, and experiments were carried out at reaction temperatures of 270–400 °C, residence times of 5–30 min, a pressure of 20 MPa, and an oil-to-1-butanol molar ratio of 1:40. The factors affecting the product yield, such as temperature and time, were investigated and discussed in detail. The result showed that the highest biodiesel yield of 94.73 mol% was achieved at 400 °C within 14 min. The detailed kinetic model describing the transesterification of canola oil in SCB agreed well with the experimental data. The corresponding reaction rate constants and activation energies were determined. In comparison to supercritical methanol, supercritical ethanol, and supercritical 1-propanol, the reactivity of SCB was the lowest.

1. Introduction

At present, global warming is one of the most concerning threats to our planet. Since reports state that global warming is caused by excessive use of fossil fuel resources, increased attention has been focused on biofuels as an alternative to replace fossil resources. Biofuels are sustainable, carbon neutral, lack sulfurous compounds, and most importantly, emit less carbon monoxide (CO) [1]; their use fully complies with the aims and purposes of environmental protection.

Biodiesel, a well-known biofuel, is derived from edible and non-edible oil [2–4], animal fats [5], or algae [6–8] through the transesterification process. Several methods have been employed to produce biodiesel with the addition of catalyst, in order to accelerate the transesterification process. These include the addition of bases [9], acids [10], or enzymes [11]. Due to use of these catalysts, many problems have been reported: (1) basic catalysts are sensitive to the presence of water and high free fatty acid (FFA), (2) acidic catalysts tend to require long reaction times, and (3) the enzyme is costly and sensitive to the solvent. Moreover, separation and purification of catalyst in the downstream process is required, thereby lengthening the production process.

Non-catalytic biodiesel production using supercritical technology was reported to circumvent problems faced by the aforementioned methods because it holds many advantages, which include no sensitivity to water and FFA, easier separation and purification, higher reaction rate, no catalyst requirement, and no wastewater generation [12,13]. Extensive studies have been conducted to produce biodiesel using this technology, with a focus on reaction characteristics [14,15], reaction kinetics [16,17], life cycle assessment (LCA), energy analysis, and feasibility [18–20]. Recently, two-step biodiesel production process from waste cooking oil has been developed: firstly FFAs are esterified catalyzed by acid as a pretreatment, and then the acylglycerols are transesterified using a homogeneous alkali catalyst [21]. This method provides a promising solution to convert feedstock with high FFA levels to biodiesel. In addition, advanced supercritical methyl acetate method for biodiesel production from non edible *Pongamia pinnata* oil with the addition of 10 wt% aqueous acetic acid has been studied [22]. It was found that high FFA content in *Pongamia pinnata* oil did not give any adverse effect on the biodiesel production process. Most recently, in-depth study of transesterification reaction of *Pongamia pinnata* oil for biodiesel production in supercritical methanol was also investigated [23]. It was found that optimal reactions conditions were found at 300 °C and 90 min reaction with almost complete triglyceride conversion.

Furthermore, most previous studies focused on biodiesel production using short-carbon-chain alcohols, such as methanol and ethanol, which have low energy contents and are hygroscopic, and are therefore corrosive [24]. Thus, the use of long-carbon-chain alcohols is preferred to produce biodiesel, i.e., 1-butanol.

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As reported by Gottumukkala et al. [25], 1-butanol is a renewable alcohol that can be synthesized from agricultural waste, such as rice straw, so that biodiesel production from canola oil in supercritical 1-butanol (SCB) is considered an environmentally friendly route. In addition, 1-butanol has higher cetane number and heating value than short carbon chain alcohols, which is more favorable for blending with biodiesel fuel. Moreover, 1-butanol has a higher miscibility in diesel due to the long carbon chain in its structure; thus, it is more appropriate for compression ignition engines [26]. Therefore, it is of great interest and practical to study the reaction behavior of biodiesel production in SCB and elucidate the reaction kinetics.

Apart from biodiesel production using supercritical methanol (SCM) and supercritical ethanol (SCE), only a few studies regarding biodiesel production with SCB have been reported. Warabi et al. [27] examined biodiesel production from rapeseed oil under supercritical alcohol conditions, including 1-butanol, using a batch reactor at 300 °C. Recently, Sun et al. [28] attempted biodiesel production in SCB from camelina oil using a micro-reactor. They reported that the cold temperature property (pour point of −19 °C) and high calorific value (HHV of 39.97 MJ/kg) made fatty acid butyl ester (FABE) an ideal liquid transportation fuel. However, no one has studied the reaction behavior in SCB using a continuous reactor. By employing a continuous reactor, the pressure can be constantly controlled, and elucidation of the reaction kinetics is much more precise than that in a batch reactor. Therefore, this study aims to investigate the reaction behavior and elucidate the reaction kinetics of the transesterification process in SCB. The factors affecting the yields of biodiesel, intermediate products of diglyceride (DG) and monoglyceride (MG), and glycerol (GL) by-product, such as temperature and time, were investigated and discussed in detail. Moreover, a model of the detailed reaction kinetics for biodiesel production in SCB was developed, and the yields of biodiesel obtained in this study were compared with those in supercritical methanol, ethanol, and 1-propanol (SCM, SCE, and SCP, respectively).

2. Materials and methods

2.1. Experimental

Biodiesel production in SCB was carried out in the temperature range of 270–400 °C under a fixed pressure of 20 MPa. The oil-to-1-butanol molar ratio was fixed at 1:40, and the transesterification reaction was performed for 5–30 min.

The details of the reactor employed in this study are presented elsewhere [29]. Briefly, this reactor was made of stainless-steel tubing (SS316), with an inner diameter of 2.17 mm and a length of 3.5 m. Feedstock was fed into the reactor using two high-pressure pumps. First, water was fed and then the reactor temperature was increased to the desired value. After achieving a constant temperature, the pressure was increased to 20 MPa by using a back-pressure regulator. Then, the canola oil and 1-butanol was fed to the reactor in place of water. The samples were then collected after a steady-state was achieved. The obtained products were removed from the reactor after passing through the heat exchanger, filter, and backpressure regulator. The obtained biofuel was a single-phase. The residence time was determined as shown in our previous report [14].

Ester yields from the experimental results were calculated by dividing the moles of biodiesel product by moles of fatty acid group in the initial triglyceride (TG) [14] as shown in this following formula.

$$(\text{Ester yield}) = \frac{(\text{Molar amount of biodiesel product})}{(\text{Molar amount of fatty acid group in initial TG})}$$

Meanwhile, yields of DG, MG, and GL were defined as the mass of corresponding product generated per initial TG mass.

2.2. Analytical methods

A gas chromatograph (GC) (GC-390B, GL Sciences) equipped with a flame-ionization detector and an MET-Biodiesel column, featuring an integrated 2-m guard column (Sigma Aldrich, 28668-U), was used to analyze the reaction products. Argon was used as the carrier gas, and the details of the analytical methods are reported elsewhere [30]. Briefly, the temperature program in the oven was as follows: 1 min at 50 °C, followed by a temperature ramp of 15 °C/min to 250 °C, at which point the temperature was held for 10 min; then, the temperature was ramped at 15 °C/min to 380 °C and maintained at this temperature for 5 min. The temperatures of the injector and detector were both set at 380 °C. Both standard and sample injection volumes were 1 μL, and peak identification was made by comparing the retention times between the standard and sample compounds. In this study, ASTM D6584 was adopted as a method to determine monoglycerides, diglycerides, and triglycerides in which tricaprin was added as the internal standard to analyze all components in synthesized biofuel. The concentrations of biodiesel, intermediate compounds of diglyceride (DG) and monoglyceride (MG), and glycerol (GL) by-product were determined using a calibration curve on the basis of peak areas.

2.3. Reagents and materials

All chemicals used in this study were of high purity and used without further treatment or purification. The canola oil feedstock used in the experiments was produced by a commercial manufacturer (J-Oil Mills, Tokyo, Japan). 1-Butanol (98%) was the product of Nacalai Tesque, Inc. (Kyoto, Japan), and the biodiesel (methyl oleate, min. 60.0%) standard was the product of Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triolein (99.9%), diolein (99.9%), and monoolein (min. 40%) standards were products of Nacalai Tesque, Inc. (Kyoto, Japan); Sigma-Aldrich, Co., (Japan); and Tokyo Chemical Industry Co., Ltd. (Japan), respectively. A glycerol (99%) standard was the product of Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). In order to prepare GC standard solutions, analytical grade tricaprin and n-hexane were used.

3. Results and discussion

3.1. Effect of temperature and time on product yield

In order to investigate the reaction behavior of transesterification of canola oil in SCB, the effects of temperature and time on the yields of biodiesel product, intermediate compounds of DG and MG, and GL by-product were studied first. Temperature, together with time, had a vital impact on product yield. In this study, transesterification was carried out at a fixed pressure of 20 MPa and an oil-to-1-butanol molar ratio of 1:40, since these were the optimum conditions for biodiesel production under supercritical alcohols, as previously reported [12,14,31].

Even though the effect of temperature and time on biodiesel production under supercritical alcohol condition are extensively investigated by many research groups, the details of these effects on product composition behavior in supercritical 1-butanol have not been studied well. The effect of temperature and time on the yield of biodiesel, DG, MG, and GL is illustrated in Fig. 1. Fig. 1(a) displays the effect of temperature and time on biodiesel yield at 270, 300, 350, and 400 °C, under a fixed pressure of 20 MPa and oil-to-1-butanol molar ratio of 1:40. At 270 °C, the biodiesel yield obtained was still relatively low. Under these conditions, the bio-