



Continuous production of biodiesel under supercritical methyl acetate conditions: Experimental investigation and kinetic model



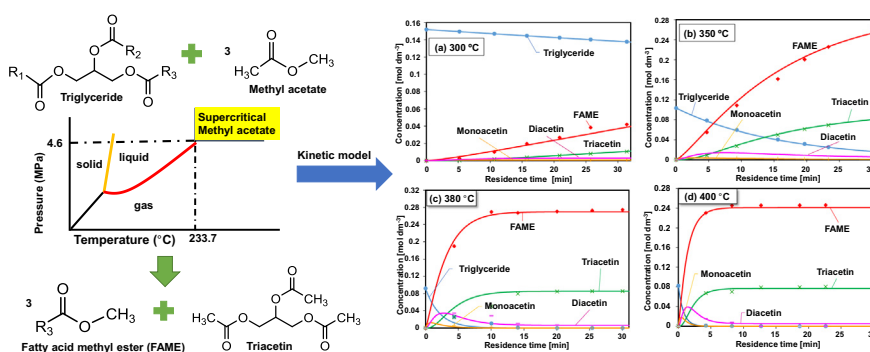
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HIGHLIGHTS

- Reaction behavior of biodiesel production in supercritical methyl acetate.
- The highest biodiesel yield was achieved at 380 °C and 20 MPa after 10 min.
- The detailed reaction kinetics for transformation of triglyceride to biodiesel.
- The kinetic model expressed good agreement with experimental data.
- Methyl acetate has low reactivity compared to alcohol and MTBE.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, biodiesel production by using supercritical methyl acetate in a continuous flow reactor was investigated for the first time. The aim of this study was to elucidate the reaction kinetics of biodiesel production by using supercritical methyl. Experiments were conducted at various reaction temperatures (300–400 °C), residence times (5–30 min), oil-to-methyl acetate molar ratio of 1:40, and a fixed pressure of 20 MPa. Reaction kinetics of biodiesel production with supercritical methyl acetate was determined. Finally, biodiesel yield obtained from this method was compared to that obtained with supercritical methanol, ethanol, and MTBE (methyl tertiary-butyl ether). The results showed that biodiesel yield with supercritical methyl acetate increased with temperature and time. The developed kinetic model was found to fit the experimental data well. The reactivity of supercritical methyl acetate was the lowest, followed by that of supercritical MTBE, ethanol, and methanol, under the same conditions.

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1. Introduction

The renewable energy field has attracted enormous research interest in recent times because of the need to slow down environmental damage and to reduce dependence on fossil fuels. Biodiesel has been well established as a promising renewable energy source as it is biodegradable, renewable, environmentally benign, and a

clean-burning substitute for petroleum and diesel (Pasqualino et al., 2006; Canakci, 2007).

Over the past few decades, biodiesel has been produced commercially using conventional catalytic reactions, either acidic or alkaline. However, these methods continue to have several drawbacks; they are time consuming, generate huge amounts of waste water, and are highly sensitive to the presence of water and free fatty acids (FFAs) (Kasim et al., 2009). In addition, the downstream separation and purification steps for the removal of impurities, such as saponified by-products and catalyst, from biodiesel are tedious (Hawash et al., 2009; Kusdiana and Saka, 2004).

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Biodiesel production by using supercritical technology could address the limitations of conventional catalytic methods, since it could be carried out without the addition of catalyst (Saka and Kusdiana, 2001). The complete conversion of oil to biodiesel can be achieved within a short residence time. Transesterification of triglycerides and esterification of FFAs occur simultaneously. The separation and purification steps are easier (Lee and Saka, 2010; Farobie et al., 2014).

Glycerol is a by-product of biodiesel production. Increasing demand for biodiesel has led to an increase in the production of this by-product, causing the price of glycerol to fall dramatically. To overcome this problem, a transesterification process that does not produce glycerol as a by-product is needed. One approach to produce biodiesel without producing glycerol is by using supercritical methyl acetate. The first paper describing biodiesel production by using supercritical methyl acetate was published by Saka and Isayama (2009). This method was reported to produce triacetin, a higher value-added product than glycerol. Since the publication of this work, several researchers have studied biodiesel production by supercritical methyl acetate by using different feedstocks such as purified palm oil (Tan et al., 2010); soybean, sunflower, *Jatropha curcas*, and waste soybean oils (Campanelli et al., 2010); *Jatropha curcas* oil (Niza et al., 2011); soybean and macauba oils (Doná et al., 2013); and rapeseed oil (Goembira and Saka, 2013).

All the aforementioned studies were conducted in batch-type tube reactors and tubular packed-bed reactors. To the best of the authors' knowledge, there has been no detailed study on reaction kinetics for biodiesel production with supercritical methyl acetate using a continuous mode-reactor. Kinetic characterization of a reaction is important for understanding the reaction behavior. The objectives of this study were to investigate the reaction behavior of biodiesel production by using supercritical methyl acetate and to elucidate its reaction kinetics using a continuous mode-reactor.

2. Materials and methods

2.1. Experimental

The transesterification process was carried out by using supercritical methyl acetate. The details of the reactor are presented elsewhere (Farobie et al., 2015). In brief, feedstock consisting of canola oil and methyl acetate was fed into the reactor by using a high-pressure pump. The pressure was then increased to 20 MPa by using a back-pressure regulator. The reactor temperature was increased to the desired value, and the samples were collected after steady state was achieved. The reaction products were removed from the reactor after passing through a filter and the back-pressure regulator. In this study, the transesterification reaction was carried out in the temperature range of 300–400 °C under constant pressure of 20 MPa for 5–30 min. The oil-to-methyl acetate molar ratio used in this study was fixed at 1:40.

Residence time τ [s] was determined by using Eq. (1), which incorporates mass flow rate of oil, w_o [kg/s]; the mass flow rate of methyl acetate, w_r [kg/s]; the density of oil, ρ_o [kg/m³]; and that of methyl acetate, ρ_r [kg/m³]; at a certain reaction temperature and pressure; and reactor volume, V [m³]:

$$\tau = \frac{V}{\frac{w_o}{\rho_o} + \frac{w_r}{\rho_r}} \quad (1)$$

2.2. Analytical methods

The products were analyzed by using a gas chromatograph (GC) (GC-390B; GL Sciences) equipped with a flame-ionization detector

and a MET-Biodiesel column featuring an integrated 2-m guard column (28668-U, Sigma Aldrich). The details of the analytical methods have been reported previously (Farobie et al., 2014).

Biodiesel yields were calculated by dividing the moles of biodiesel product by the moles of the fatty acid group in the initial triglyceride (TG), as shown in Eq. (2). Furthermore, the product concentration was calculated by using a peak area-based calibration curve.

$$\text{Product yield} = \frac{\text{mol of biodiesel product}}{\text{mol of fatty acid group in initial TG}} \quad (2)$$

2.3. Reagents and materials

All chemicals used in this study were of high purity and were used without further treatment and purification. The canola oil feedstock used in this study was produced by a commercial manufacturer (J-Oil Mills, Tokyo, Japan). Methyl acetate (99%) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). The following standard compounds were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan): methyl oleate (min. 60.0%), methyl linoleate (min. 98.0%), methyl linolenate (min. 95.0%), methyl palmitate (min. 97.0%), methyl stearate (min. 95.0%) diacetin (min. 40%), and monoacetin (>40%). Triolein (99.9%) and triacetin (98%) standards were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Analytical grade tricaprln and *n*-hexane were used to prepare standard solutions for GC.

3. Results and discussion

3.1. Effect of temperature and time on biodiesel yield

The reaction behavior and yield of biodiesel using supercritical methyl acetate method was studied by varying the duration and temperature of the reaction. Fig. 1 shows the changes in the concentration of triglycerides, biodiesel product, monoacetin, diacetin, and triacetin at 300, 350, 380, and 400 °C. In all cases, high temperature and long reaction times allowed the completion of transesterification and thus increased biodiesel yields. This result agrees well with those of other supercritical methods used for producing biodiesel (Farobie and Matsumura, 2015a, 2015b; Tsai et al., 2013; Velez et al., 2012).

At 300 °C, biodiesel yields were relatively low even after 30 min of reaction. At this temperature, biodiesel yields were merely 0.08 and 0.09 mol/mol (concentration of 0.0383 and 0.0419 mol dm⁻³) after transesterification times of 25 and 30 min, respectively. The concentration of monoacetin and diacetin were relatively constant. Triacetin production tended to increase with time.

At 350 °C, the conversion of canola oil to biodiesel was higher than that at 300 °C, but the complete conversion of canola oil to biodiesel could not be achieved even after 30 min. Biodiesel yields of approximately 0.60, 0.70 and 0.83 mol/mol (concentration of 0.207, 0.2258 and 0.2638 mol dm⁻³) were obtained after transesterification times of 20, 25, and 30 min, respectively. In the case of supercritical methanol and ethanol, 350 °C is optimal for the transesterification process, since complete conversion of oil to biodiesel could be achieved within 10 and 30 min with supercritical methanol and ethanol, respectively (Farobie and Matsumura, 2015a; Madras et al., 2004; Silva et al., 2007; Warabi et al., 2004).

At 380 °C, a substantial change in conversion of canola oil to biodiesel was observed at a reaction time of 10 min. Biodiesel yields of approximately 0.96 and 0.97 mol/mol (concentration of 0.2673 and 0.2705 mol dm⁻³) were obtained after transesterification times of 15 and 20 min, respectively. At this temperature, the concentration of intermediate compound, monoacetin and dia-

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