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A novel spiral reactor for biodiesel production in supercritical ethanol

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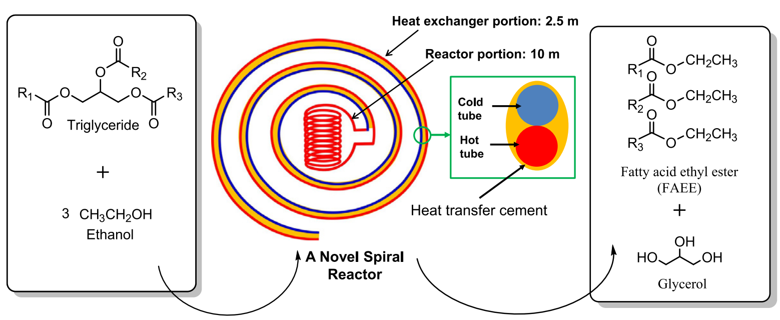
HIGHLIGHTS

- A novel spiral reactor for biodiesel production in supercritical ethanol was proposed.
- The spiral reactor employed in this study successfully recovered heat.
- The effects of temperature and time on FAEE yield were investigated.
- FAEE yield as high as 0.937 mol/mol was obtained at 350 °C after 30 min.
- The second-order kinetic model expressed the experimental yield well.

GRAPHICAL ABSTRACT



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ABSTRACT

A spiral reactor is proposed as a novel reactor design for biodiesel production under supercritical conditions. Since the spiral reactor serves as a heat exchanger, it offers the advantage of reduced apparatus space compared to conventional supercritical equipment. Experimental investigations were carried out at reaction temperatures of 270–400 °C, pressure of 20 MPa, oil-to-ethanol molar ratio of 1:40, and reaction times of 3–30 min. An FAEE yield of 0.937 mol/mol was obtained in a short reaction time of 30 min at 350 °C and oil-to-ethanol molar ratio of 1:40 under a reactor pressure of 20 MPa. The spiral reactor was not only as effective as conventional reactor in terms of transesterification reactor but also was superior in terms of heat recovery. A second-order kinetic model describing the transesterification of canola oil in supercritical ethanol was proposed, and the reaction was observed to follow Arrhenius behavior. The corresponding reaction rate constants and the activation energies as well as pre-exponential factors were determined.

1. Introduction

Some researchers have investigated biodiesel production by transesterification of triglycerides through various methods such as homogeneous [1–3] and heterogeneous acid-alkali treatments [4–8] as well as enzyme catalysts [9]. All of these mentioned methods have their challenges and drawbacks such as soap formation, longer reaction time, pre-treatment requirements, lower reaction rates, and strict reaction conditions. To circumvent these problems, Saka and Kusidana [10–12] have proposed a method for biodiesel production via the non-catalytic transesterification of oil under supercritical alcohol conditions, which enjoys some advantages such as higher reaction rates, applicability to various feedstock chemicals, no waste water generated, easier separation, no catalyst requirement, and high biodiesel yields [10,11]. Nevertheless, heat recovery in this process is problematic in terms of its commercial application. The heat recovery problem can be solved using continuous-flow reactor. However, in some previous studies [13–18] employing continuous-flow reactor for biodiesel production in supercritical ethanol, the heat exchanger or condenser or cooling system should be built up separately. Thus, it still remains the

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drawback toward commercialization due to the high cost of apparatus.

To overcome this problem, we propose a new spiral reactor, which is composed of a parallel tube heat exchanger and high-temperature transesterification reactor. The parallel tube heat exchanger, where heat is recovered, is in turn composed of two tubes placed side-by-side in a spiral formation. The high-temperature transesterification reactor, where the reaction mainly takes place, consists of insulated tubing. In addition, since the spiral reactor employed in this study could serve as the heat exchanger at once, this reactor design has the advantages of reducing the required space as well as low cost compared to conventional reactors. Conventional shell-and-tube or plate-type heat exchanger get very bulky and costly when designed to hold high pressure. Conventional double tube heat exchanger is difficult to fabricate and again costly. The advantage of cheap and space-saving heat exchanger is what is actually sought for the commercialization of this high temperature and high pressure biodiesel production.

The main goal of this study is to obtain the fundamental characteristics of this spiral reactor for biodiesel production under supercritical ethanol conditions. For this purpose, the most important factors affecting biodiesel yield, namely temperature and reaction time, were studied. The novel findings of this work highlight the utility of the as-described spiral reactor as a novel reactor for biodiesel production under supercritical ethanol conditions, which, to the best of the knowledge of these authors, is not available in the literature. Ethanol was selected as a reactant in this study since it can be derived from renewable resources [19–22]. In addition, biodiesel obtained from ethanol-fatty acid ethyl esters (FAEEs)-has a higher cetane number and heating value compared to fatty acid methyl esters due to the greater number of carbon atoms contained in ethanol [23,24].

2. Material and methods

2.1. Experimental

The transesterification reaction was carried out in supercritical ethanol using the spiral reactor. The experimental apparatus used in this research is schematically illustrated in Fig. 1. The apparatus consisted of a pump, spiral reactor, ceramic micro heater, heat transfer cement, thermal insulator, thermocouples, filter, and back-pressure regulator.

A detailed schematic of the spiral reactor is shown in Fig. 2. The spiral reactor consisted of 1/8 inch piping made of stainless-steel tubing (SS316) with an inner diameter of 2.17 mm. It was composed of heat exchanger portion and the reactor portion. The heat exchanger portion made of two tubes placed side by side and fixed by the heat transfer cement (Thermon, T-99). The flow in these tubes were countercurrent flow so that heat exchange was conducted from one tube to another efficiently. The length of the reactor portion was 10.0 m and that of the heat exchanger was 2.5 m. Seven thermocouples from T1 to T7 were equipped to measure the real temperature inside spiral reactor. These thermocouples were installed for the cold and hot tubes of heat exchanger part (two thermocouples) at the reactor length of 0, 1.25, 2.5 m, respectively, and one thermocouple was installed at the reactor length of 7.5 m in the center. The length of reactor part from inlet heat exchanger tube which has length of 2.5 m (T3) to the reactor part which has length of 7.5 m (T4) is 5.0 m, and the length of reactor from the reactor part (T4) to the outlet of heat exchanger part (T5) is 5.0 m as well. Therefore, the total length of reactor part is 10.0 m. Meanwhile, for the heat exchanger part, the length of 2.5 m is calculated from the parallel tube of T1–T7 to T3–T5. These thermocouples were connected with a union tee fitting. Inlet and outlet arrows show the inflow and outflow of effluent, respectively.

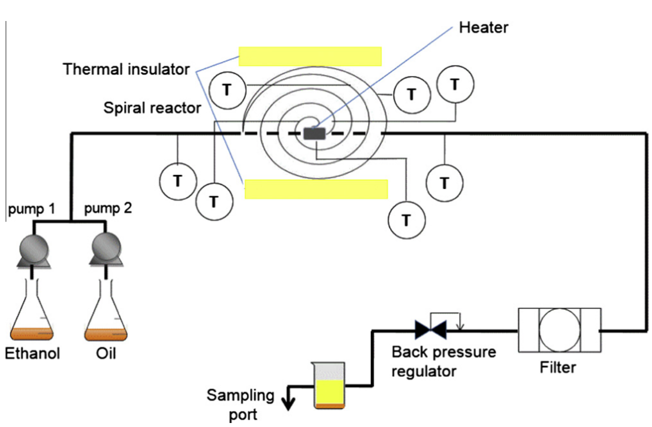

Fig. 1. Experimental apparatus.

A mixture of canola oil and ethanol was fed through the heat exchanger portion to the reactor portion at the desired temperature. The inlet flow was heated by exchanging heat with the effluent flow. Since complete heat recovery is not possible, additional heat was supplied to the reactor from the ceramic micro heater (Sakaguchi, MS-1000R). This ceramic micro heater was installed in the reactor portion (center part).

In this study, the transesterification reaction was carried out in the temperature range of 270–400 °C at a pressure of 20 MPa since the critical temperature and pressure of ethanol are 241.56 °C and 6.268 MPa, respectively [25]. In addition, some previous studies reported that optimum condition of biodiesel production in supercritical ethanol could be achieved at 20 MPa [13–16,26,27]. The molar ratio of oil to ethanol used in this study was fixed at 1:40 since some references [13,28] reported that the optimum molar ratio of oil to reactant for biodiesel production under supercritical conditions is 1:40. The transesterification reaction was performed for reactor residence time ranging from 3 to 30 min, and samples were obtained after achieving a steady state. The obtained products were removed from the reactor after passing through the filter and back-pressure regulator. All measurement and sampling were made more than 1 h after the desired reaction condition was achieved, making sure that steady state was reached. All experimental runs were conducted in triplicate, and the average was taken.

Residence time was determined using Eq. (1), assuming there is not volume change caused by mixing. Product concentration was calculated using calibration curve on the basis of peak area. This residence time was adopted as reaction time in this study. The reactor volume here is the volume for reactor portion which has the length of 10.0 m.

$$\text{Residence time[min]} = \frac{\text{reactor volume}[\text{dm}^3]}{\frac{\text{mass flow rate of oil[g/min]}}{\text{density of oil}[\text{g/dm}^3]} + \frac{\text{mass flow rate of ethanol[g/min]}}{\text{density of ethanol}[\text{g/dm}^3]}} \quad (1)$$

FAEE yields from the experimental results were calculated by dividing the moles of product FAEE by moles of fatty acid group in the initial TG as shown in Eq. (2).

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