Energy Conversion and Management 124 (2016) 212–218

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

New insights in biodiesel production using supercritical 1-propanol

Obie Farobie [a], Zi Yan Michelle Leow [b], Thachanan Samanmulya [a], Yukihiko Matsumura [a,*]

[a] Division of Energy and Environmental Engineering, Institute of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan
[b] Department of Mechanical Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:
Received 27 May 2016
Received in revised form 5 July 2016
Accepted 8 July 2016
Available online 18 July 2016

Keywords:
Biomass
Biodiesel
Continuous process
Supercritical fluids
1-Propanol

ABSTRACT

In this study, for the first time, continuous biodiesel production and the related reaction kinetics in supercritical 1-propanol (SCP) were investigated. This study aims to investigate the reaction characteristics of biodiesel production using SCP and to elucidate the kinetics. The experimental conditions were as follows: temperature, 270–400 °C; residence time, 5–30 min; a fixed pressure of 20 MPa; and an oil-to-1-propanol molar ratio of 1:40. A model of the detailed reaction kinetics for biodiesel production in SCP was developed, and the biodiesel yields obtained in this study were compared with those in supercritical methanol and ethanol (SCM and SCE). The result showed that the biodiesel yield in SCP increased with temperature and time. The detailed kinetic model was found to agree well with the experimental data. The reactivity of SCP was lower than that of SCM and SCE. The activation energies for the conversion of triglyceride to diglyceride, diglyceride to monoglyceride, and monoglyceride to glycerol were about 111.39, 78.99, 60.96 kJ mol^{-1}, respectively.

1. Introduction

The high concerns surrounding global warming have triggered many researchers to look for a better, alternative source of renewable energy. Biodiesel fuel is said to be the next promising bioenergy that could replace conventional diesel fuel because of its attractive carbon neutral properties, which help in reducing the greenhouse gas emission profile. In addition, biodiesel has many advantages over petro-diesel fuel, such as low toxicity and high biodegradability [1], low aromatic and sulfur contents [2], as well as low particulate matter, total hydrocarbon, and carbon monoxide (CO) emissions [3]. Furthermore, it is comparable with commercial diesel fuel in terms of cetane number and soot formation [4,5].

At present, biodiesel is mostly produced using alkali-catalyzed transesterification. Unfortunately, over the past few years, many problems related to this process have been reported. One of the major drawbacks is the need to remove both the catalyst and the saponified product from free fatty acids after the reaction [6]. The purification process of free fatty acids tends to prolong the production and thus result in further complications. Supercritical technology is considered as one of the best alternative methods to produce biodiesel. This technology offers many advantages such as applicability to various feedstocks, higher reaction rate, and easier separation; in addition, the process requires no catalyst and does not generate wastewater [7–9].

Up to now, many studies have been conducted on biodiesel production using supercritical methanol and ethanol (SCM and SCE), with focus on the reaction behavior [10–13], reaction kinetics [14–16], and energy analysis [17]. Besides, new approaches for glycerol-free biodiesel production using supercritical methyl acetate [18,19], dimethyl carbonate [20], and *tert*-butyl methyl ether [21–23] have been extensively studied. Moreover, an innovative approach to produce biodiesel has also been carried out via injection of non-catalytic superheated methanol technology in which the solvent was heated beyond the critical temperature but the reactor pressure remained at atmospheric pressure [24,25].

Considering that the low-carbon alcohols methanol and ethanol are hygroscopic and corrosive and have low energy content [26], it is desirable to use higher-carbon alcohols, such as 1-propanol. 1-Propanol can be produced commercially, via petrochemical as well as fermentative processes, from glucose by using metabolically engineered *Escherichia coli* via the keto-acid pathway [27]. In addition, nowadays, 1-propanol can be produced not only from D-glucose but also from L-rhamnose and glycerol. Even from the viewpoint of carbon yield in the fermentation process, 1-propanol is advantageous over ethanol in that it can be produced from glucose without CO_2 formation, whereas the biosynthetic pathway using ethanol includes CO_2 emission steps [28]. Hence, the use of 1-propanol as a reaction medium for biodiesel production offers good future prospects.

* Corresponding author.
E-mail address: mat@hiroshima-u.ac.jp (Y. Matsumura).

http://dx.doi.org/10.1016/j.enconman.2016.07.021
0196-8904/

As opposed to reactions in methanol and ethanol media, biodiesel production in supercritical 1-propanol (SCP) has been studied to a very limited extent. Only Warabi et al. [29] have attempted biodiesel production under supercritical conditions using alcohols, including 1-propanol, in a batch reactor. Nonetheless, their reaction temperature was limited to 300 °C. Furthermore, the reaction kinetics of biodiesel production using SCP have not been investigated in detail. Therefore, the purpose of this study is to investigate the reaction behavior of biodiesel production in SCP and to elucidate the reaction kinetics. The factors that contributed to the biodiesel yield, namely, temperature and residence time, were also studied.

2. Materials and methods

2.1. Experimental

Transesterification was carried out in SCP using the continuous flow reactor schematically illustrated in Fig. 1. The reactor was made of stainless-steel tubing (SS316), with an inner diameter of 2.17 mm and a length of 3.5 m. The feedstock consisting of canola oil and 1-propanol was fed into the reactor by using a high-pressure pump, and then, the pressure was increased to 20 MPa by using a backpressure regulator. The reactor temperature was increased to the desired value, and the samples were collected after steady state was achieved. The obtained products were removed from the reactor after they were allowed to pass through the filter and the backpressure regulator. In this study, transesterification was carried out in the temperature range of 270–400 °C under a fixed pressure of 20 MPa for 5–30 min. The oil-to-1-propanol molar ratio was fixed at 1:40. The residence time was determined as shown in our previous paper [15].

2.2. Analytical methods

The products were analyzed 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 (Sigma-Aldrich, 28668-U). Peak identification was achieved by comparing the retention times between the standard and sample compounds. Tricaprin was used as an internal standard and the concentrations of TG, DG, MG, and by-product were calculated using a calibration curve on the basis of peak areas.

The details of the analytical methods have been reported previously [21]. In addition, biodiesel yields were calculated from the experimental results by dividing the number of moles of the biodiesel product by the number of moles of the fatty acid group in the initial triglyceride (TG), as presented elsewhere [15].

2.3. Reagents and materials

All chemicals used in this study were of high purity and were 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-Propanol (98%) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Biodiesel (methyl oleate, min. 60.0%) standard was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triolein (99.9%), diolein (99.9%), and monoolein (min. 40%) standards were purchased from Nacalai Tesque, Inc. (Kyoto, Japan), Sigma-Aldrich Co. (Japan), and Tokyo Chemical Industry Co., Ltd. (Japan), respectively. Glycerol (99%) standard was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). To prepare GC standard solutions, analytical grade tricaprin and *n*-hexane were used.

3. Results and discussion

3.1. Effect of temperature and residence time

First, the effects of temperature and time on the biodiesel yield were studied to investigate the reaction behavior of biodiesel production in SCP. Fig. 2 shows the effect of temperature on the biodiesel yield in SCP. Overall, the biodiesel yield increased with temperature and time, since high temperatures and long reaction times allowed the completion of the transesterification process. This result is consistent with previous work involving supercritical biodiesel production methods, according to which the conversion of oil to biodiesel increased as the temperature was increased from 200 to 400 °C [11,15,21,30].

The effect of residence time on the concentrations of TG, biodiesel product, intermediate compounds monoglyceride (MG) and diglyceride (DG), and by-product glycerol was further investigated in detail. As observed in Fig. 3, at 270 °C, the conversion of canola

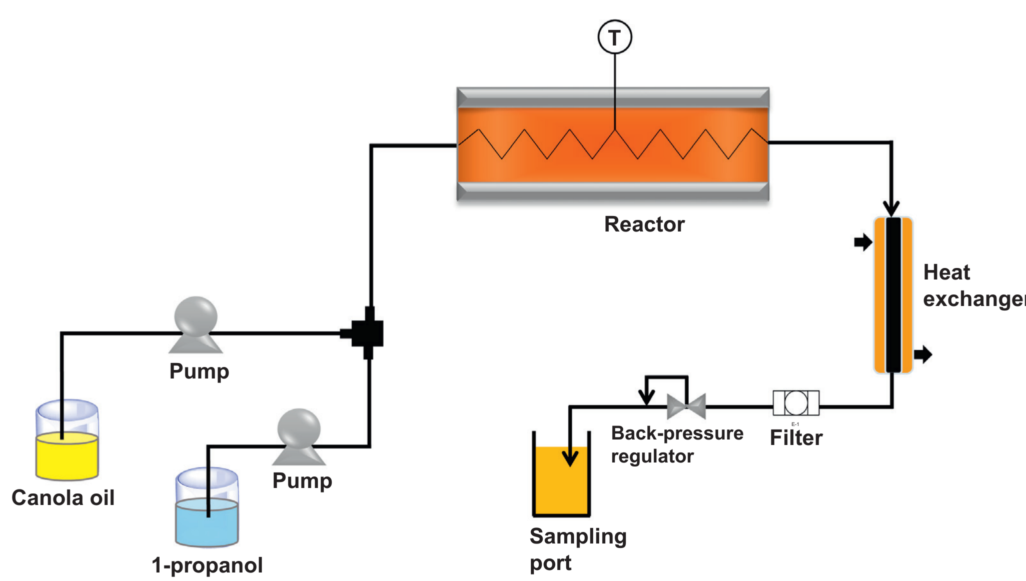

Fig. 1. Schematic diagram of experimental apparatus.