



Continuous esterification of oleic acid to ethyl oleate under sub/supercritical conditions over γ -Al₂O₃



Jiuxu Liu, Yue Nan, Xinlei Huang, Jesse Q. Bond, Lawrence L. Tavlarides*

Department of Biomedical and Chemical Engineering, Syracuse University, 329 Link Hall, Syracuse, NY, 13244, United States

ARTICLE INFO

Keywords:

Esterification
Oleic acid
Subcritical and supercritical conditions
 γ -Al₂O₃

ABSTRACT

Esterification of oleic acid with ethanol was conducted under subcritical and supercritical conditions in a packed-bed reactor containing γ -Al₂O₃. The presence of γ -Al₂O₃ significantly improved the reaction rate such that the 42% yield achieved at 325 °C, 200 bar, and 1-min residence time without the alumina was increased to 98% at the same conditions when alumina was present. The catalytic capacity was attributed to Lewis acid sites on the surface of alumina, and non Brønsted acid sites were detected. Experiments to study the kinetics were executed at a pressure of 200 bar, elevated temperatures (200, 225, 275, 300, and 325 °C), and residence times of half to 8 minutes. Mass transfer limitations were estimated to be negligible via the Mears and Weisz-Prater criteria. Kinetic analysis based on the one-step model demonstrates that the overall reaction was endothermic, and an Eley-Rideal (ER) reaction mechanism was proposed to describe each elementary reaction step. The stability of γ -Al₂O₃ on product conversion was tested via a 25 h operation under 325 °C, 200 bar, and 1 min residence time, and decrease of the conversion was not observed. However, results of the catalyst analytical characterization shows a decrease of the acid site density and surface area, supporting the occurrence of catalyst degradation. The addition of water slightly decreased the yield, while the pressure change from 200 to 100 bar did not have an obvious effect on the conversion.

1. Introduction

Considerable amounts of wastewater is generated in biodiesel industry in order to remove the dissolved homogeneous catalysts from the product [1,2]. Plus, the production cost of biodiesel is expensive, since current industry uses refined oils including soybean, palm, and rapeseed oil as the feed stocks considering that the homogeneous catalysts are sensitive to the presence of free fatty acids and water which are present in cheap low-quality oils [3]. These problems could be solved via subcritical and supercritical reaction conditions (SC). The SC conditions are created by increasing the reaction temperature and pressure to values near or above the critical point of the alcohol. Under such severe conditions, the properties of alcohol are changed such as density of hydrogen bonding in alcohols significantly decreases, and alcohols become nearly non-polar [4,5,6]. These changes contribute to the mixing of alcohols and oils to have the reactions performed in a homogeneous reaction phase which minimizes mass transfer resistance and therefore significantly increases the reaction rate. The high reaction temperatures also benefit the reaction rate. Due to the fast reaction rate under SC conditions, it is possible to perform the reactions non-catalytically, which eliminate the contamination problem as mentioned

above. Additionally, the SC method could be more economically competitive compared to current industrial technology [7,8], since it can directly use low-quality and low-cost oils and hydrous alcohols [9–11].

However, biodiesel fuel will be thermally decomposed when temperatures exceed 350 °C [12,13], which further degrades fuel qualities [14–16]. In order to complete the SC reactions at temperatures lower than 350 °C in short reaction times to avoid decomposition reactions, one can add catalysts into the SC reaction media. Some researchers showed that a near complete yield was reached at 225 °C, 200 bar and 5 minutes by adding trace amount of strong basic homogeneous catalysts [17]. Stable heterogeneous (solid) catalysts are also expected to provide a similar product yield under SC conditions.

Solid catalysts can be acidic or basic. The popular basic catalysts include hydroxides, dolomites, hydrotalcites, mixed basic metal oxides, loaded and supported alkaline elements and oxides, which are commonly used under conventional conditions in biodiesel synthesis. In specific, CaO-based compounds including pure CaO [18] and loaded CaO [19,20], and potassium-based compounds including loaded KF [21], KI [22], and KOH [22] have drawn numerous attention due to their high activity and wide availability. Other alkaline metal oxides such as MgO [23], ZnO [24] and SrO [24] have also been studied by

* Corresponding author.

E-mail addresses: jliu23@syr.edu (J. Liu), lltavlar@syr.edu (L.L. Tavlarides).

different researchers. Even though high product yields were reached by applying these basic catalysts, serious leaching problems were found and the active compounds were detected in biodiesel product with high concentrations even at mild conditions. The acidic catalysts to synthesize biodiesel include acidic metal oxides [25], sulfated/tungstated metal oxides [26–30], sulfonic ion-exchange resin, heteropolyacids, zeolites, and etc. Since the catalytic capacity of the acidic solids is lower than solid bases, the reactions with the acids were executed under more severe conditions. Similarly, most of the acidic solids were not stable under the reaction conditions due to leaching and other issues, despite high yields were achieved initially.

A literature review indicates that several synthesized compounds were found to be relatively stable even at temperatures higher than 190 °C including Zr-SBA-15 [31], ZnAl_2O_4 [32], and $\text{ZnO-TiO}_2\text{-Nd}_2\text{O}_3/\text{ZrO}_2$ [33]. Zr-SBA-15 (mixture of zirconia and mesoporous silica) was tested by Melero et al. [31] in a packed-bed reactor at 210 °C, 70 bar, and residence time of 30 min for which the reaction yield reached 96% with negligible catalyst leaching. Biodiesel yield of 70% was obtained at 210 °C and 4 h reaction time in a batch reactor containing ZnAl_2O_4 reported by Pugnet et al. [32]. Zinc leaching was very low that no more than 4 ppm by weight was detected in the ester phase after 6 h of contact time. By conducting the reactions in a packed-bed reactor over $\text{ZnO-TiO}_2\text{-Nd}_2\text{O}_3/\text{ZrO}_2$ at 200 °C and 69 min residence time, 95% biodiesel yield was reported by Kim et al. [33], and the leaching of ZnO was determined to be negligible by ICP analysis.

Some simple and largely available metal oxides such as titania, zirconia and alumina have been commonly used as catalyst supports due to their thermal and mechanical stability even at SC conditions. However, they did not show any catalytic ability under conventional conditions ($T = 70$ °C, ambient pressure) due to their weak acidic properties. McNeff et al. [34] reported that under SC conditions, reactions with alumina, zirconia, and titania, reached conversions over 90% at 360 °C and 200 bar. However, the temperatures proposed were too severe, which degraded biodiesel. Due to the very limited information, the optimal SC conditions for biodiesel production over the simple metal oxides are still unknown.

Generally speaking, information regarding synthesizing biodiesel fuel under SC conditions with heterogeneous catalysts is very limited. Besides, kinetics of the alcoholysis with heterogeneous catalysts under SC conditions are rarely reported in the literature, although kinetic studies for biodiesel production at conventional conditions with heterogeneous catalysts have received much attention over the past few decades [35–44].

Accordingly, this study aims to (1) explore the possibility of converting free fatty acids, which largely exist in waste cooking oils and animal tallows, to biodiesel fuel under SC conditions at short residence times over alumina powder, and (2) to study the kinetics for the catalytic reaction systems, neither of which is well addressed in the literature. The reactions were performed in a packed-bed reactor containing $\gamma\text{-Al}_2\text{O}_3$ under SC conditions (temperature from 200 to 325 °C, and pressure from 100 to 200 bar). Oleic acid was employed to represent all free fatty acids that could exist in cheap oils. Although methanol is preferred in biodiesel industry considering its cheaper cost, in this study ethanol was chosen as the alcohol instead of methanol, since ethanol has a better solubility with oleic acid than methanol. The improved solubility will benefit the mixing of reactants and minimize the mass transfer resistance. The reactions of methanol-based biodiesel synthesis should share the same mechanism of ethanol-based biodiesel due to the similar chemical and physical properties of the two alcohols.

2. Experimental

2.1. Material

Anhydrous ethanol (200 proof, 100 vol%) was purchased from Pharmco-Aaper. Oleic acid, GC analytical standards for oleic acid and

ethyl linoleate, white quartz (50 + 70 mesh), *n*-methyl-*n*-(trimethylsilyl) trifluoroacetamide (MSTFA) (GC derivatization synthesis grade), and pyridine were purchased from Sigma Aldrich. *n*-Heptane (HPLC grade) was provided by Thermo Fisher Scientific. Deactivated glass wool used in reactor packing was purchased from Restek Corporation. Gases (ultrahigh purity grade) used in GC, FTIR, and TPD analysis were supplied by Airgas. $\gamma\text{-Al}_2\text{O}_3$ was provided by Acros in neutral form.

2.2. Catalyst characterization

The fresh catalyst were tested at 150 °C under vacuum for 10 h, and it was found negligible mass change. This suggests high purity of the catalyst, and the moisture and other deposit on the fresh catalyst was negligible. Accordingly, no further treatment was applied, and the fresh catalyst was directly used in the esterification reactions.

Powder XRD investigation was performed using a Bruker D8 Advance ECO powder diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 25 mA with a step size of 0.02 in the 2 θ angle range of 15–70°.

Scanning electron microscope (JEOL) was utilized to physically observe the morphology of the fresh and spent catalyst.

N_2 adsorption-desorption isotherms were conducted by Micromeritics ASAP 2020 (adsorption of N_2 at 77 K). Prior to N_2 dosing, samples were degassed under vacuum (423 K, 8 h). Brunauer-Emmett-Teller (BET) and t-plot analyses were used to determine total and micropore surface areas. Barrett-Joyner-Halenda (BJH) analysis of the adsorption branch of N_2 isotherms was used to determine pore size distributions and average pore diameters. Pore volumes were calculated from cumulative nitrogen uptake at a relative pressure of 0.99.

Density of Lewis acid sites was determined from temperature programmed desorption (TPD) of ammonia [45]. Typically, approximately 70 mg of sample was inserted into a 1/2 inch quartz tube between two quartz wool (Grace) end plugs and the whole tube was further placed in an Omega furnace. The temperature of the furnace was regulated by a process controller (Love, series 16 A) and monitored by a type K thermocouple (Omega). All samples were calcined (4 h, 723 K, 3 K/min) under air flow (50 scm^3/min) before analysis. After cooling to 423 K, samples were purged in dry He flow (100 scm^3/min) for more than 90 min. Catalysts were further dosed with ammonia (1% ammonia and 1% argon, Airgas) flow. After saturation of ammonia on the surface, physically adsorbed ammonia was removed by applying a high He flowrate (400 scm^3/min) for at least 1 h. The furnace was then ramped to 973 K (10 K/min) under He including 1% Ar serving as an internal standard. Chemisorbed ammonia was removed after ramping. During the whole process, a mass-selective residual gas detector (Stanford Instruments RGA 100) was used to track MS signals of ammonia ($m/z = 16$) and Ar ($m/z = 40$) in the effluent.

Brønsted acid sites to Lewis acid sites ratio was determined using pyridine FTIR (Nicolet 6700 DTGS detector). 15–25 mg of catalysts were pressed into a 13 mm pellet through a hydraulic press. The pellet was loaded on an in-situ cell, designed and built in house. Samples were calcined as the procedure described before. Subsequently, the cell was cooled to 423 K, and purged under a flow of 60 scm^3/min of He gas. The He was purified by a liquid nitrogen trap followed by a moisture trap. The pellet was then dosed with 4 torr of pyridine (Sigma Aldrich, 99%). After the pellet was fully saturated, the cell was purged under a He flow of 200 scm^3/min at 423 K to remove physically adsorbed pyridine. Spectra were collected at 423 K. and Brønsted to Lewis ratios were determined by the ratio of the integrated IR bands at 1545 cm^{-1} (pyridinium ion) and 1455 cm^{-1} (pyridine) respectively, by applying the appropriate molar extinction coefficients [46] However, the prime quantities of interest in this study are Lewis site densities since no Brønsted acid sites was detected. The operation procedures for FTIR and TPD can be also found as described in prior publications, respectively [47,48].

Download English Version:

<https://daneshyari.com/en/article/6498372>

Download Persian Version:

<https://daneshyari.com/article/6498372>

[Daneshyari.com](https://daneshyari.com)