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Transforming duck tallow into biodiesel via noncatalytic transesterification

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HIGHLIGHTS

- Non-catalytic transforming triglyceride into biodiesel.
- Non-catalytic esterification of free fatty acids (FFAs).
- Enhanced biodiesel conversion under the presence of CO_2.
- Non-catalytic biodiesel conversion via the continuous flow system.
- High tolerance of the amount of free fatty acids.

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ABSTRACT

The transformation of the lipids extracted from duck tallow into biodiesel was achieved using activated alumina and CO_2 under ambient pressure (1 bar). Crude fatty acids (~98% assay) were also esterified to help us understand and validate the noncatalytic biodiesel conversion mechanisms. Its conversion efficiency was nearly 93.5(±0.5)%. The transformation of crude fatty acid into biodiesel proves that this newly developed technology for the production of biodiesel combines esterification of free fatty acids and transesterification of triglycerides into a single process that has a 98.5(±0.5)% conversion efficiency to biodiesel within 1 min at 350–500 °C. This paper addresses the simplest methodology for the production of biodiesel. Herein, it is confirmed that the main driving force of biodiesel conversion in the noncatalytic transesterification reaction is temperature rather than pressure. Noncatalytic biodiesel transformation can be achieved in the presence of a porous material via a thermochemical process in a continuous flow system. This noncatalytic biodiesel transformation was enhanced under the presence of carbon dioxide (CO_2).

1. Introduction

There are diverse reasons to explore the use of vegetable oil as a substitute for petroleum-derived fuel, such as the limited and fast-diminishing reserves of petroleum-derived oil, increasing prices of crude oil, and environmental concerns [1–3]. Biofuels have been drawing increasing attention as alternative fuels owing to their environmental benefits [4–10]. Among the renewable and sustainable biofuels, biodiesel based on vegetable oil has the key advantage of being able to use existing distribution networks and current diesel fuel engine technology [11–14]. The use of biodiesel enhances energy security, because it can be derived from renewable and domestic sources [7,15].

Direct use of triglycerides has not been satisfactory because of their high viscosity and poor ignition properties [14,16]. Treatments that could overcome the major problems associated with the high viscosity of vegetable oils when used as diesel engine fuels include dilution, microemulsification, pyrolysis, and transesterification with alcohols of short chain lengths [17,18]. Transesterification of triglycerides with alcohol leads to the formation of less viscous fatty alkyl esters, which are commonly known as biodiesel.

Despite the bright prospect of biodiesel as a sustainable source of energy, efforts to commercialize it have been very limited throughout the world. One of the major obstacles is the high price

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of refined vegetable oil as feedstock, which makes up nearly 70% of the total production costs [7,19–21]. Hence, in order to reduce the cost of biodiesel, waste or low-quality fats, which are inexpensive and readily available, could be utilized as feedstock. However, the challenge in employing cheap feedstocks such as waste oils, inedible oils, and animal fats is the presence of impurities such as water and free fatty acids (FFAs), which are common components in waste fats [22–27]. In addition, economically viable biodiesel conversion technology must also be developed.

Currently, biodiesel is mainly produced in the industry via the transesterification reaction using triglycerides and methanol in the presence of homogeneous catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) [10,20,28,29]. Although these base catalysts are relatively cheap, they are very sensitive to FFAs and the water content in oils, since the side reactions of saponification and hydrolysis, respectively, can occur [30]. It is well known that the conventional catalytic processes used for biodiesel production cannot efficiently use inexpensive lipid feedstocks without additional pretreatment steps, which add to the processing costs. Acid-catalyzed processes appear to tolerate high FFA contents in refined vegetable oils and fats, but the excessively long time required to achieve a high yield of biodiesel and the dilution of the catalyst by warm water in the feedstock hinder scale-up of these processes [31,32].

Thus, the limitations of homogeneous catalytic reactions have driven researchers to focus on alternative technologies in biodiesel production, such as biodiesel production via transesterification with a heterogeneous catalyst under subcritical conditions and noncatalytic synthesis under supercritical conditions [6,33–36]. In particular, the application of supercritical methanol technology has been getting a lot of attention lately. For example, biodiesel production under supercritical conditions has a higher tolerance for water and FFAs, as solid catalysts suffer from the adverse effect of deactivation when exposed to oils containing high amounts of water [37,38]. However, this promising technology has an obvious disadvantage in its high operating temperature and pressure [10]. For example, noncatalytic conversion under supercritical conditions is usually carried out at temperatures above 250 °C, pressures higher than 100 bars, and a methanol-to-oil molar ratio of 42:1 compared to the stoichiometric ratio of 3:1 [34,35].

The main objective of this work was to develop and mechanistically validate the simple noncatalytic transesterification process for converting duck tallow into biodiesel via a thermochemical process in a continuous system under ambient pressure. This noncatalytic biodiesel conversion was mechanistically validated with crude oleic acid. In addition, this work proved that noncatalytic biodiesel conversion could be achieved in an efficient manner by using only activated-alumina (Al_2O_3) and carbon dioxide (CO_2). This work also aimed to clarify the optimal operational conditions such as temperature, pressure, and feeding ratio of raw material for noncatalytic biodiesel conversion.

2. Method and materials

2.1. Sample preparation and material purchase

Duck tallow was obtained from a local slaughterhouse (Gwangju, South Korea) and restaurant (Gwangyang-City, South Korea). Duck tallow was exracted with n-hexane (Dae-Jung Chemical, Incheon, South Korea). A rotary evaporator was used to recover nonpolar solvent (Cole-Parmer, Vertical, 115VAC, USA). Crude fatty acid was purchased from Samchun pure chemical Co., Ltd. (Pyeontaek, Korea). Crude fatty acid contains various fatty acids, but the most abundant are in the C_{16-18} range of fatty acids, such as hexadecanoic acid and oleic acid. Among them, oleic acid is dominant (~70%). The lipids extracted from duck tallow were characterized by the acid value (AV). AV is expressed as the amount of KOH in mg necessary to titrate all the FFAs contained in 1 g of oil. The AV is determined by the following equation: $AV = V \times c \times 56.11/m$, where V is the volume of KOH solution used to titrate sample (ml), c is the concentration of the KOH solution (mol L^{-1}), and m is the sample mass.

Activated alumina (Dae-Jung Chemical, Incheon, South Korea) was used for the experiment. Activated alumina was characterized in terms of surface area (297.350 $m^2 g^{-1}$) and pore distribution (average pore diameter: 5.4112 nm) using a BELSORP-mini II (BEL Japan Co., Ltd.). The activated alumina was visualized using a scanning electron microscope (SEM; Hitachi VP-SEM S-3400N, Japan). The pore distribution and SEM image of the activated alumina used for the experiment are shown in Fig. SM-1.

2.2. Experimental setup

A tubular reactor (TR) made of 1-inch outer diameter (od) quartz tubing (Chemglass ® CGQ-0800T-13) and a 1-inch Stainless Ultra-Torr® Vacuum Fitting (Swagelok SS-4-UT-6-400) was used. Activated alumina was packed into the reactor. The required experimental temperature in the range 250–500 °C was achieved using a split-hinged tubular-type furnace (AsOne, Japan); the temperature was simultaneously monitored by an S-type thermocouples to ensure that the target temperature had been met. An insulation collar (high-temperature Duraboard insulation) at the end of the furnace was used to block heat transfer during operation and to protect the quartz tubing. Oil feedstock and MeOH were continuously introduced into the tubular reactor using a gear pump (micro annular gear pump MZR-2905, Germany) and a high-performance liquid chromatography (HPLC) pump (Lab Alliance PN #F40SFX01, USA).

All gases used in the experiments were of ultrahigh purity and obtained from Daesung Industrial Gases Co., Ltd. All gas flow rates were set using Brooks mass flow controllers (Brooks SLA5800 Series). A computer-aided control system with LabVIEW (National Instruments, USA) was employed.

After the reaction, the mixture was allowed to settle for 2 h before the glycerin layer and top layer including the biodiesel (FAME) fraction were separated, subsequently removed into separate bottles, and weighed and analyzed via gas chromatography–mass spectrometry (GC/MS; HP-7890A/5975C MSD). The GC/MS and GC/flame ionization detector (FID) instruments were calibrated with the Supelco FAME mixture (Lot # LB-80557). The DB-WAX (J&W 127-7012) and HP-5MS (19091S-413E) GC columns were employed. The EN14103 method was used for the FAME conversion.

3. Results and discussion

3.1. Thermal characterization of duck tallow

A series of thermo-gravimetric analysis (TGA) tests was carried out. The initial experiments were carried out at a heating rate of 10 °C min^{-1} over a temperature range from ambient temperature to 900 °C under N_2. Representative thermograms from a series of TGA experiments with duck tallow (acid value: 29.12) and crude fatty acid are shown in Fig. 1. Fig. 1(a) shows approximately 13% of residual. However, the crude fatty acid shows virtually no residual mass in Fig. 1(b).

The thermogram of duck tallow shows a slight mass decay of approximately 1.85% in the temperature regime between 99 °C and 132 °C. This mass decay can mainly be attributed to moisture content in the duck tallow, which is evidenced by the differential