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Evaluating the effectiveness of various biochars as porous media for biodiesel synthesis via pseudo-catalytic transesterification

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HIGHLIGHTS

- Sustainable biodiesel production by using biochar with a high yield.
- Optimization of pseudo-catalytic transesterification temperature on biochar.
- Pseudo-catalytic biodiesel yield on biochar sensitive to lignin content of biomass.

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ABSTRACT

This study focuses on investigating the optimized chemical composition of biochar used as porous material for biodiesel synthesis via pseudo-catalytic transesterification. To this end, six biochars from different sources were prepared and biodiesel yield obtained from pseudo-catalytic transesterification of waste cooking oil using six biochars were measured. Biodiesel yield and optimal reaction temperature for pseudo-catalytic transesterification were strongly dependent on the raw material of biochar. For example, biochar generated from maize residue exhibited the best performance, which yield was reached ~90% at 300 °C; however, the maximum biodiesel yield with pine cone biochar was 43% at 380 °C. The maximum achievable yield of biodiesel was sensitive to the lignin content of biomass source of biochar but not sensitive to the cellulose and hemicellulose content. This study provides an insight for screening the most effective biochar as pseudo-catalytic porous material, thereby helping develop more sustainable and economically viable biodiesel synthesis process.

1. Introduction

Searches for alternative fuels have recently increased in consequence of the rapid depletion of fossil fuel reserves and the unprecedented global environmental issues such as climate change. In addition, the increase in supply cost of fossil fuels in line with political uncertainty (McGlade and Ekins, 2015) have become another driving force for finding alternative fuels. Among various alternative fuels (fuel cells, biofuels, hydrogen, refuse-derived fuel, *etc.*), biodiesel becomes one of the most widely used alternative fuels since it can be produced from various resources from terrestrial biomass (*i.e.*, edible and inedible lipid) from aquatic biomass (*i.e.*, microalgal lipid) (Boyle, 2012). In addition, technical and environmental benefits of using biodiesel in current diesel engines is that it has greater lubricity and lower sulfur content than petro-derived diesel (Khiari et al., 2016).

Biodiesel is made up of fatty acid alkyl esters that are commonly synthesized by transesterification between a vegetable oil, microalgal oil, or animal fat and an anhydrous short-chain alcohol in the presence of catalyst. A large number of homogeneous and heterogeneous catalysts have been developed for biodiesel production (Canakci and Gerpen, 1999; Dias et al., 2012; Nanda et al., 2014). Homogeneous base catalyzed transesterification (*e.g.*, NaOH and KOH) has a fast reaction rate at moderate conditions (*e.g.*, ambient pressure: 1 bar and 60–63 °C) (Lotero et al., 2005); however, this process requires refined lipid feedstocks (*i.e.*, low content of free fatty acids (FFAs) and moisture) because free fatty acids and moisture provided a favorable route for saponification (*i.e.*, soap formation) with base catalyst rather than transesterification (Meher et al., 2006). Even though homogeneous acid catalyzed transesterification (*e.g.*, H_2SO_4) is less sensitive to the purity of feedstock than base

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catalyzed reaction, it generally suffers from slow reaction rate, waste generation from neutralization, and equipment corrosion (Di Serio et al., 2007; Goff et al., 2004). Also, product separation from the same phase catalyst is always challenging in homogeneous catalytic transesterification (Enweremadu and Mbarawa, 2009). In these respects, heterogeneous catalytic transesterification has been preferred as an alternative way to synthesize biodiesel due to an easy catalyst separation (Abbaszaadeh et al., 2012). However, insecure durability at harsh reaction conditions (*i.e.*, high reaction temperature and pressure) and high cost of such catalysts are considered as demerits (Kostić et al., 2016; López et al., 2007). In addition, transesterification with a supercritical alcohol has been studied to produce biodiesel in absence of any catalyst (Tan et al., 2009). In spite of giving a high biodiesel yield without catalyst, the supercritical transesterification requires high temperature (250–450 °C) and pressure (200–400 bar) rendering the process expensive (Balat and Balat, 2008). Therefore, it is very desirable to establish a new platform for biodiesel synthesis process without using catalyst in ambient pressure.

From this point of view, a new concept of transesterification, namely called pseudo-catalytic transesterification, has been proposed by the authors (Jung et al., 2016c; Kwon et al., 2012), which is thermally induced in the presence of a catalytically inert porous material such as silica. For example, heating reactants (an alcohol and lipids) results in two different phases during transesterification (*i.e.*, gaseous alcohol and liquid lipids exist at the same time by the difference in boiling point). These two-phase reactants collide each other in numerous pores on porous media, making a similar effect of catalyst lowering activation energy of transesterification. The pseudo-catalytic conversion of triglycerides gave a high yield of fatty acid methyl esters (~96%) on silica in absence of catalyst at ambient pressure (Jung et al., 2016c). However, conventional porous materials such as silica are generally not inexpensive, also a high reaction temperature (*e.g.*, ~400 °C) was required to reach the high yield of fatty acid methyl ester (FAME) (Jung et al., 2016a). Thus, it should be developed cheaper and more environmentally benign porous materials in order to enhance sustainability in biodiesel production. Among various candidates for sustainable and inexpensive porous material, biochar can be used as surrogate porous medium in pseudo-catalytic transesterification.

Biochar has recently been highlighted as a sustainable porous material used for carbon capture and sequestration, environmental remediation, and fuel cell electrodes (Ahmad et al., 2014; Mohan et al., 2014; Rajapaksha et al., 2016; Woolf et al., 2010; Yuan et al., 2015), produced by the thermal degradation (*i.e.*, pyrolysis) of biomass (Lee et al., 2017). The pore structure and physicochemical properties of biochar can be modified by changing the kind of biomass and pyrolytic conditions, treating biomass and/or biochar (Rajapaksha et al., 2016). However, there is no literature studying the use of biochar for pseudo-catalytic processes, for instance, biodiesel production.

In these respects, this study aims to find effective and inexpensive biochar as a potential porous medium for pseudo-catalytic transesterification. To do this, this study evaluated the effectiveness of six different biochars generated from various biomasses (maize residue, pine cone, rice husk, Japanese wood, mixed wood, and bamboo) as surrogate porous medium for pseudo-catalytic transesterification of waste cooking oil and methanol. For example, the trends of biodiesel yield as a function of reaction temperature by applying each biochar were extracted to find the most effective biochar for the pseudo-catalytic synthesis of biodiesel. In addition, we correlated the yield of biodiesel with holocellulose (*i.e.*, cellulose and hemicellulose) and lignin contents in the source of the biochars to provide a fundamental screening tool for the selection of biochar as a new sustainable porous material of pseudo-catalytic production of biodiesel.

2. Materials and methods

2.1. Materials

Methanol (99.9%) and dichloromethane (⩾99.9%) were purchased from Daejung Chemicals (Siheung, Korea) and from Sigma-Aldrich (St. Louis, MO, USA), respectively. Waste cooking oil was collected from a local restaurant. Properties of the oil were examined by Research Institute of Petroleum Technology, Korea (Table S1).

2.2. Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) of waste cooking oil was conducted using a Mettler Toledo TGA star unit (Columbus, OH, USA). The TGA experiment was performed from 30 to 900 °C at a heating rate of 10 °C min^{-1}. A 10 ± 0.1 mg of sample was loaded for TGA test. Ultra-high-purity nitrogen was used as purge and protective gas and the gas flow rate (60 mL min^{-1}) was controlled by mass flow controllers embedded in the TGA system.

2.3. Production and characterization of biochar

Rice husk, maize residue, pine cone, and bamboo were collected from agricultural fields in Korea. Mixed wood and Japanese wood were obtained from a biomass recycling center. These samples were dried and chopped (average particle size: 1 mm) prior to pyrolysis in N_2 at 450 °C (heating rate: 7 °C min^{-1}) for 3 h in a box furnace. Surface area, pore volume, pore size, and pore distribution of the biochars were measured by N_2 physisorption at −196 °C using a Micromeritics ASAP 2010. Prior to N_2 physisorption, the samples were degassed at 120 °C for 12 h. A Hitachi S-4300 field emission-scanning electron microscope (FE-SEM) was used to characterize morphology of the biochars. Contents of volatile matter, fixed matter, moisture, and ash were measured as described in the literature (Ahmad et al., 2013). Holocellulose and lignin contents of the biomass were analyzed as described elsewhere (Pettersen, 1984).

2.4. Biodiesel production and analysis

A 0.2 mL of waste cooking oil, 10 mL of methanol, and 200 mg of a biochar were loaded in a bulkhead union (SS-400-61, Swagelok). Both ends of the bulkhead were sealed with plugs (SS-400-P, Swagelok). The sealed bulkhead was heated by a temperature-programmable furnace at a ramping rate of 30 °C min^{-1}. A GC-FID (Varian-450) equipped with an Agilent DB-Wax column was used for analysis of biodiesel. Ultra-high-purity N_2 was used as a carrier gas (flow rate: 30 mL min^{-1}). A sample was diluted 30-fold in dichloromethane prior to injection. The column setting followed: 1) held at 50 °C for 3 min, 2) heated to 180 °C at 10 °C min^{-1}, 3) held at 180 °C for 5 min, 4) heated to 230 °C at 5 °C min^{-1}, and 5) held at 230 °C for 28 min. Calibrations of FAMEs were performed using a standard mixture of FAMEs (47885-U, Sigma-Aldrich). Quality assurance/quality control in the GC-FID are shown in Supporting information (Table S2).

3. Results and discussion

3.1. Characteristics of biochar

Table 1 summarizes the properties of biochars produced from different biomass feedstocks. The composition of biochar was highly contingent on its original biomass. Compared to other biochars, the ash contents of maize residue (42.0 wt.%) and rice husk