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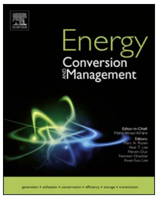

Sustainable approach to biodiesel synthesis via thermally induced transesterification using biochar as surrogate porous media

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ABSTRACT

This study validates whether maize residue biochar could be used as surrogate porous media for thermally induced transesterification of waste cooking oil. The highest yield of fatty acid methyl esters (FAMEs) reached up to 91% at 300 °C with the biochar while it reached at 380 °C with silica. This suggests that energy saving can be expected using biochar in the biodiesel production process. Larger pore size and wider pore distribution of the biochar likely provides favorable conditions for the high biodiesel yield at lower temperature than silica. Based on similar FAME yields between refined soybean oil and waste cooking oil, the thermally induced transesterification with the biochar exhibited an extraordinary tolerance against impurities in waste cooking oil.

1. Introduction

Due to the diminished reserves of fossil fuels and global warming, there have been the scientific and engineering research efforts to produce economically viable alternative fuels from renewable resources. Among alternative fuels, biodiesel which is composed of mono alkyl esters of long-chain fatty acids (FAs) has taken center stage in substituting petro-diesel. Indeed, biodiesel has been blended with petro-diesel for transportation fuel in many countries. For example, BD20 (20% biodiesel blended with petro-diesel) is the most common biodiesel blend in USA [1]. In addition, biodiesel consumption in USA has increased from 260 million gallons to 1476 million gallons in 2010 and 2015, respectively [1].

It has been shown that biodiesel reduces CO_2 emissions compared to petro-diesel on a life cycle basis [2]. Also, not only does biodiesel contain no sulfur but also provides greater lubricity than petro-diesel, thereby enhancing the longevity of engines [3–5]. Biodiesel is commonly derived from a range of vegetable oils and animal fats [6–10]. The feedstocks for biodiesel production are made of complex mixtures of triglycerides (TGs) and free fatty acids (FFAs) [11]. The TGs can be converted into fatty acid methyl esters (FAMEs) via catalytic or non-catalytic transesterification. For catalytic transesterification, homogeneous base catalysts such as sodium hydroxide and potassium hydroxide are commonly adopted due to higher reaction rate. However, FFAs in feedstock can react with the base catalysts forming soap which consumes catalyst during reaction [12,13]. Transesterification over homogeneous acid catalysts such as sulfuric acid requires a large amount of alcohol and its reaction rate is slower than base catalysts [14,15]. Moreover, the homogeneous processes need water to neutralize or remove the catalyst from downstream of the transesterification process, generating a large amount of wastewater causing a high operational cost. To overcome these disadvantages, heterogeneous catalysts, such as supported metal catalysts (*e.g.*, Ni, Zn, Ag, Ce, and La) [11], solid acid catalysts (*e.g.*, sulfate zirconia, zeolite, and ion-exchange polymer resins) [16–22], carbon solid acid or base catalysts [23–26], and biocatalyst (*i.e.*, enzyme) [10], have been extensively studied for transesterification. However, heterogeneous catalyzed reactions suffer from catalyst deactivation. The cost and reusability of heterogeneous catalysts also remains as a critical issue for their commercialization [27]. Transesterification reactions occurring in supercritical conditions do not require homogeneous/heterogeneous catalysts and give a high yield of biodiesel [28]. However, the supercritical processes require high building and operation costs to withstand and maintain such harsh reaction conditions (temperature: 250–450 °C, pressure: 200–400 bar) [29]. Therefore, it is desirable to develop an inexpensive, efficient, and environmentally benign transesterification process for biodiesel production from low-cost feedstocks.

To overcome these challenges on homogeneous/heterogeneous catalyzed and supercritical processes, we have developed thermally induced esterification in the presence of a porous material, such as silica [30]. In the reaction, a certain temperature makes liquid lipids and gaseous methanol exist together. These reactants having different

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phases collide each other in numerous pores on the porous material. The collision frequency could be accelerated by externally heating. The thermally induced process with a porous material does not require any homogeneous or heterogeneous solid acid/base catalyst. Also, no high pressure was needed to initiate the thermally induced reaction. However, silica is an expensive and non-sustainable material, and a high temperature (*e.g.*, 400 °C) was needed to obtain a high yield of products (~97%) [31]. Therefore, it is highly desirable to further develop more energy-efficient (*i.e.*, a lower temperature needed for getting a high yield) and sustainable thermally induced process by using a new class of porous materials.

In this regard, herein, we used a maize residue biochar as a substitute for silica. The difference in biodiesel production with the biochar and silica was compared using waste cooking oil as the biodiesel feedstock. In addition, it was reasoned why these two porous materials show different performance. This study should provide a sustainable option for biodiesel production. More importantly, it may provide new insight for biochar applications beyond environmental remediation and soil amendment.

2. Materials and methods

2.1. Materials

Waste cooking oil was collected from a restaurant at Sejong University in Seoul, Korea. The properties of the waste cooking oil are presented in Table 1. Research Institute of Petroleum Technology, Korea examined the oil properties. Soybean oil was purchased from a local market. Methanol (99.9%) was purchased from DaeJung Chemicals & Metals. Silica and methylene chloride (≥99.9%) was purchased from Sigma-Aldrich.

2.2. Production and characterization of maize residue biochar

Maize residue was collected from the agricultural field in Korea. The maize residue was dried, chopped and pyrolyzed in a N_2 atmosphere at 450 °C (heating rate: 7 °C min^{-1}) for 180 min in a muffle furnace. Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume, size, and distribution of the maize residue biochar were measured by N_2 physisorption at −196 °C using a Micromeritics ASAP 2010. The samples were degassed at 393 K for 12 h prior to the physisorption analysis. The morphology of the biochar was characterized using a Hitachi S-4300 field emission-scanning electron microscopy (FE-SEM) equipped with an energy-dispersive X-ray spectrometry (EDS). Proximate and ultimate analyses of the biochar were performed by the methods described in previous literature [32].

Table 1
Properties of the waste cooking oil used in this study.

Property		Value
Viscosity at 40 °C ($mm^2 s^{-1}$)		38.54
Density at 15 °C ($kg m^{-3}$)		926.5
Carbon residue (wt.%)		0.47
N content (wt.%)		0.003
S content (wt.%)		0.009
P content ($mg kg^{-1}$)		27.750
V content ($mg kg^{-1}$)		0.305
Water content (wt.%)		0.108
Ash content (wt.%)		0.006
Alkali metal ($mg kg^{-1}$)	Na	4.806
	Ca	0.811
	K	4.289
Gross heating value ($kcal kg^{-1}$)		9372
Acid value (mg of KOH g^{-1})		2.85
Iodine value ($g g^{-1}$)		1.16

2.3. Thermally induced transesterification and FAME analysis

For the thermally induced thermally induced transesterification, methanol (0.2 mL) and waste cooking oil (10 μL) and biochar (200 mg) were loaded in a bulkhead (Swagelok), followed by sealing both ends. The sealed bulkhead was in a temperature-programmable furnace. The temperature inside the bulkhead was monitored using a K-type thermocouple. The bulkhead was held for ~1 min at a target reaction temperature. After reaction, the bulkhead was chilled with cold water. For recovering FAMEs, liquid products and biochar were mixed with methylene chloride allowing that all FAMEs are dissolved in the solvent. To ensure the reproducibility, all the experiment was triplicated. Prior to the injection into GC (Varian 450) equipped with Agilent DB-Wax column, the sample was diluted 30-fold in methylene chloride. The column was first held at 50 °C for 3 min and then heated to 180 °C (10 °C min^{-1}). After 5 min holding at 180 °C, it ramped up to 230 °C (5 °C min^{-1}) holding for 28 min. Ultra-high purity N_2 was used as a carrier gas with a flow rate of 30 mL min^{-1}. A commercial FAME mixture purchased from Sigma-Aldrich was used for FAME calibrations in the GC. The detailed information on the multiple calibrations were provided in Supporting information. The biodiesel yield was calculated in relation to the total weight of waste cooking oil used (Eq. (1)).

$$\text{Biodiesel yield (\%)} = 100 \times \frac{\sum \text{mass of each FAME (g)}}{\text{mass of waste cooking oil (g)}} \qquad (1)$$

3. Results and discussion

3.1. Characterization of silica and maize residue biochar

Table 2 summarizes the characterization results of silica and the maize residue biochar. Surface area and total pore volume of silica is 81 and 62 time higher than those of the biochar, respectively. However, average pore size of the biochar is almost 2 times greater than that of silica. The biochar has a high ash content (39.2 wt.%) likely resulting from a high mineral content of maize residue. The amount of fixed carbon is higher than one of volatile matter. The biochar also contains 4.37 wt.% of moisture.

Pore size distribution of silica and the maize residue biochar is shown in Fig. 1. The two porous materials show a different pattern of pore size distribution. The most pores range from 6 to 8 nm for silica while those range from 18 to 36 nm for the biochar. In addition, clearly, silica has a narrower pore distribution than the biochar. Silica mostly has mesopores, but the biochar has both mesopores and macropores.

Table 2
Characterization of silica and the maize residue biochar.

	Silica	Maize residue biochar
BET surface area ($m^2 g^{-1}$)	451.10	5.54
BJH total pore volume[a] ($cm^3 g^{-1}$)	0.88	0.014
BJH average pore diameter[a] (nm)	5.98	17.34
Proximate analysis		
Moisture (wt.%)	–	4.37
Volatile matter (wt.%)	–	12.69
Fixed carbon (wt.%)	–	43.74
Ash (wt.%)	–	39.20
Ultimate analysis		
C (wt.%)	–	77.94
H (wt.%)	–	3.09
O (wt.%)	–	16.75
N (wt.%)	–	2.01
S (wt.%)	–	0.21
H/C[b]	–	0.47
O/C[b]	–	0.16

[a] From BJH desorption.
[b] Molar ratio.