



Functionalization of biochar derived from lignocellulosic biomass using microwave technology for catalytic application in biodiesel production



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ABSTRACT

A study to produce an efficient catalyst to be used for biodiesel production was carried out introducing sulfonic groups in biochar using a microwave reactor. The transesterification reaction of waste cooking oils using the catalyst was also evaluated in a microwave reactor. The results showed that an increase in the temperature up to 140 °C during biochar sulfonation enhanced the SO₃H content on the catalyst surface. These results were confirmed through FT-IR and XPS analyses. A reduction in the surface area of the biochar was observed during the sulfonation. An increase of SO₃H groups on the biochar surface was responsible for a higher FAME yield close to 90%. The catalyst could be re-used for up to six cycles by washing with hexane.

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1. Introduction

Functionalization of biochar is attracting much attention for heavy metal removal from waters, as a catalyst for hemicellulose hydrolysis, and in catalytic applications for biodiesel production [1–4].

Biodiesel, or fatty acid methyl ester (FAME), is widely considered to be an attractive sustainable fuel obtained by esterification or transesterification of different raw materials using basic or acid catalysts. Several conventional and non-conventional basic-catalyzed transesterification processes have been reported. According to Ejikeme et al. [5] the most widely used process for transesterification of vegetable oils is alkaline catalysis (using NaOH or KOH). However, according to Kulkarni and Dalai [6], the use of alternative raw materials with high acidity (waste cooking oil for example) with this type of catalyst may promote a secondary saponification reaction; this produces certain disadvantages, including low conversion rate, low biodiesel quality and high operational cost [5,7,8].

An alternative to solve this problem is the use of acid catalysts. The use of solid acid catalysts for biodiesel production has been already proposed, including tungstated zirconia [9,10], metal oxides [11,12], carbon based acid catalyst [3,4,13–15], etc. Compared to sulfuric acid, these catalysts can reduce the possibility of emulsion formation, not only maintaining a high biodiesel yield but also simplifying catalyst recovery after the reaction.

A carbon based acid catalyst can be developed by sulfonation of a carbonaceous material, however this process needs long reaction times and high temperatures. For example, Dehkoda et al. [14] and Yu et al. [3] reported two carbon-based solid acid catalysts prepared by biochar sulfonation with concentrated or fuming sulfuric acid at a temperature of 150 °C and reaction times between 5 and 15 h. Kastner et al. [15] described the synthesis of acid catalysts by sulfonating biochar using concentrated H₂SO₄ at 100, 150 and 200 °C for 12 h and also using gaseous SO₃ at 23 °C for 6 days. In addition, the use of these solid carbon-based acid catalysts in the esterification reaction of fatty acids for biodiesel production is typically completed (~90–100% conversion) within 30–60 min in the presence of excess methanol at temperatures between 55 and 60 °C (10).

Microwave irradiation can promote shorter reaction times for both carbonaceous material sulfonation and lipids transesterifica-

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tion. Microwave irradiation can heat the reactants directly and therefore reach the reaction temperature in a shorter time [16,17]. Besides avoiding the wall effect in heat transfer, microwave reactors can also reduce overall energy consumption since energy is transferred directly through the reaction mixture [18,19].

Very recently, microwave irradiation has been explored in novel biodiesel production processes [16–18,20]. However, this technique has not been tested yet for biochar functionalization and subsequent lipid transesterification.

The objective of this research was to develop a reusable, porous, biochar-based acid catalyst for use in biodiesel production from waste cooking oil by microwave irradiation and subsequent transesterification.

2. Materials and methods

2.1. Biochar production

A pilot-scale electric pyrolyzer designed at the University of La Frontera was used to produce biochar by slow pyrolysis from oat hull. The operational variables were a temperature of 600 °C, residence time of 3 h and temperature increment rate of 3 °C/min. The characteristics of the biochar produced are shown in Table 1.

2.2. Catalyst synthesis

Biochar was slightly ground and sieved using a 150 µm mesh size; the fraction smaller than 150 µm was selected for experiments conducted subsequently. The biochar-based catalyst samples were prepared using concentrated sulfuric acid (98%, Merck) to incorporate sulfonic groups (SO₃H) onto the carbon surface. Biochar sulfonation was carried out in a microwave reactor (CEM Discover) at 100 and 140 °C for 30 min. In order to avoid collateral reactions due to energy release by the sulfonating process (exothermic reaction), CEM system may quickly reduce the overall reaction temperature in a short period of time by injection of an air flow. The sulfuric acid to biochar ratio was set at 10:1 and the sulfonation reaction was carried out in triplicate. Sulfonated biochar samples were then washed by filtration with distilled water until no sulfate was detected in the filtrate by turbidimetry (using BaCl₂). Finally the sample was dried in an oven at 105 °C overnight.

2.3. Catalyst characterization

Specific surface area (BET), pore volume (BJH), and pore size distribution were determined using a NOVA 1000e porosimeter (QUANTACHROME) by adsorbing and desorbing nitrogen at 77 K on samples previously dried and out-gassed at 160 °C for 16 h.

Fourier transform infrared (FT-IR) spectroscopy was conducted to characterize the surface functional groups using an Agilent Cary 630 FTIR diamond ATR. The total acidity (Ba(OH)₂ method) was determined according to [21].

Ultimate analysis of sulfonated biochar samples was performed using an elemental analyzer (Elemental analyzer CHNS, Eurovector EA 3000).

A variable pressure scanning electron microscope (VP-SEM) Hitachi SU 3500 was used to compare the microstructure of the catalysts produced. Backscatter Electron (BSE) in compositional mode was used to analyze the surface of each sample under operating conditions of 10 kV and 40 Pa.

X-ray photoelectron spectroscopy (XPS) spectra were obtained using a hemispherical analyser (Physical Electronics 1257 system). A twin anode (Mg and Al) X-ray source was operated at a constant power of 200 W using Al K α radiation (1486.6 eV) for the XPS measurements. The sample was placed in a sample stage in which the emission angle can be varied. In this case, the emission angle was 45°.

2.4. Biodiesel production

Waste cooking oil (WCO) was obtained from a local restaurant. Fatty acid composition of the oil determined from capillary GC analysis was 45.41% linoleic, 25.87% oleic, 5.05% palmitic, 3.73% stearic and 1.6% correspond to others acid. Oil density was 910 g/cm³, viscosity 37.2 mm²/s, acid value 3.21 mg KOH/g, water content 0.35% and iodine value 123 mg I₂/g¹⁰⁰.

WCO and methanol as acyl acceptor were used for biodiesel synthesis. Preliminary tests were performed in a microwave reactor at 100 and 140 °C for 30 min. The methanol to oil molar ratio used was 10:1 and the catalyst load was 10% based on the initial amount of oil. All assays were carried out in triplicate.

2.4.1. Kinetic studies

Subsequently, reaction kinetic trials were conducted in a microwave reactor at 140 °C for 5, 10, 15, 20, 25, 30, 40, 45, 50, 55 and 60 min at the same conditions before described.

A kinetic model was used to describe the transesterification reaction; this model considered the formation of three moles of biodiesel (FAME) and one mole of Glycerol (Gl) from one mole of triglyceride (TG) in presence of methanol (MeOH) and synthesized catalyst (K)



The transesterification reaction follows a pseudo-first order, because the reaction occurs in excess of methanol. The reaction can be expressed by a first order kinetic model in function of FAME conversion as is showed by Eq. (2).

$$r = \frac{dX_{FAME}}{dt} = k \cdot X_{FAME} \quad (2)$$

where X_{FAME} indicate the molar fraction of FAME obtained. From the integration of Eq. (2) was assumed that the initial molar fraction of FAME at time $t = 0$ is X_{FAME_0} and increases to X_{FAME_t} at time t . The integration of Eq. (2) is expressed by Eq. (3) as follow:

Table 1

Physicochemical properties of biochar pyrolyzed at 600 °C (B600) and catalysts using microwave reactor at 100 °C (BS100) and 140 °C (BS140) for 30 min.

| Sample | Specific surface area (m ² /g) ^a | Pore size (nm) | Pore volume (cm ³ /g) | C (%) | N (%) | H (%) | S (%) | H/C | Total acidity (meq/g) |
|--------|--|----------------|----------------------------------|-------|-------|-------|-------|-------|-----------------------|
| B600 | 49.32 | 1.04 | 0.008 | 81.60 | 1.14 | 2.03 | n.d | 0.025 | n.d. |
| BS100 | 30.59 | 2.30 | 0.055 | 70.63 | 1.30 | 1.98 | 2.91 | 0.028 | 3.74 ± 0.66 |
| BS140 | 5.43 | 1.03 | 0.008 | 66.31 | 0.83 | 1.99 | 7.55 | 0.030 | 7.00 ± 1.18 |

n.d: not detected.

B600: Biochar derived from oat hull by slow pyrolysis at 600 °C. BS100: Biochar sulfonated with concentrated H₂SO₄ in microwave reactor at 100 °C for 30 min. BS140: Biochar sulfonated with concentrated H₂SO₄ in microwave reactor at 140 °C for 30 min.

^a Brunauer, Emmett and Teller (BET).

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