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Research paper

Steam activation and mild air oxidation of vacuum pyrolysis biochar

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ABSTRACT

The objective of this paper was the investigation of steam activation and mild air oxidation of biochar produced by using the Pyrovac Inc. vacuum pyrolysis for a biomass feedstock composed of a 20% volume fraction of (spruce and fir) with pine (stem of Pinus strobus without bark), with a moisture mass fraction of 10%. The biochar was activated at 900 °C under a steam partial pressure of 53 kPa over 60 min. The steam activated sample was then submitted to a mild oxidation process through a reactor fed with 164 $cm^3\ min^{-1}$ of air at 200 °C under 100 kPa total pressure for 60 min. Biochar was also submitted to this mild oxidation process under the same conditions except for the oxidation time which was either 30 or 60 min. The samples were analyzed using techniques including proximate and elemental analysis, Brunauer-Emmett-Teller (BET) analysis for surface area and pore size distribution by non-local density functional theory (NLDFT), scanning and transmission electron microscopy (SEM/EDX and TEM), Boehm titration, Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). The BET surface area was increased from 50 to 1025 $m^2\ g^{-1}$ upon steam activation while the concentration of functional groups was extensively decreased. Upon mild air oxidation, the concentration of functional groups in biochar was increased from 44 to 104.6 μmol m^{-2} in oxidized biochar. Combined elemental analysis and XPS results indicated that mild air oxidation generated a more uniform spatial distribution of oxygenated functional groups than in the biochar.

1. Introduction

Biomass as the most sensible renewable source for production of energy and bioproducts, provides feasible alternatives to fossil fuels and their products [1,2]. Pyrolysis is a common method of converting biomass to several products including bio-oil, syngas, and biochar. Among these products, biochar, produced in a higher yield in slow pyrolysis, is a valuable product that has received growing attention due to its numerous applications [1–5].

Biochar can be applied as an adsorbent, catalyst or catalyst support, and for soil improvement. As adsorbent, the biochar is used to reduce number of contaminants in water such as cations or dyes. Biochar which originally dates back to “Terra Preta” (very ancient dark and fertile artificial soil found in the Amazon Basin), provides a good solution for soil quality improvement owing to its cation exchange capability, even though this improvement is not clearly established yet [4–7]. Catalytic applications of biochar are noticeable, not only due to its ability to reduce metal oxides but also because of the high surface area and porosity of activated biochar and their effects on adsorption [6,7].

Generally, in the pyrolysis process, biochar is made by the high-temperature decomposition of biomass in absence or in presence of oxygen in minor concentration. This product requires some modification including activation and oxidation depending on the targeted applications. Thus, biochar may be activated for application requiring high surface area or oxidized to create surface functional groups when polarity is needed on its internal and external surfaces [4,6–9]. The quality of activated biochar depends on the activation method as well as the type of precursor, temperature, and the type of pyrolysis process. Commonly, two approaches are used for activation. The first one is physical activation in which agents such as CO_2 and steam are applied, and the second one is chemical activation using chemicals such as KOH, H_3PO_4, and $ZnCl_2$ [6–12]. Oxidation is performed using gaseous oxidizing agents such as air or oxygen under mild temperature conditions. Other wet chemicals such as H_2O_2, H_2SO_4, $KMnO_4$, $Fe(NO_3)_3$, and H_3PO_4 have also been used [11,13–26].

The objective of the present work is to investigate the oxidation of biochar with the aim of increasing the concentration of oxygen-containing surface functional groups by using air under mild temperature conditions. This treatment is expected to increase the surface density of carboxylic functional groups thus increasing the biochar cation exchange capacity. This would make the material useful in all applications based on this parameter such as metal ion adsorption from wastewater. Mild oxidation is defined as oxidation conducted at a

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temperature below 300 °C because the burn-off, a crucial economic parameter, can be controlled [18–21,27]. Boehm titration, total reflective Fourier transform infrared spectroscopy (ATR-FTIR), elemental analysis (CHN), and X-ray photoelectron spectroscopy (XPS) were used to establish the effect of oxidation on biochar and compare its effects on external surface and bulk properties [27]. Moreover, the biochar was activated physically by steam to modify the surface morphology and develop the specific surface area and pore volume. For this purpose, different activation times and temperatures were applied and optimized to reach acceptable yield and high surface area. The resulting activated biochar was characterized by several techniques including BET analysis, pore size distribution (NLDFT), SEM/EDX, and TEM. The activated product was also oxidized since some functionalized activated biochar has been shown to be effective cation adsorbents and catalysts [15].

2. Material and methods

2.1. Materials preparation

Nitrogen (99.99%) and extra dry air cylinders were purchased from Praxair Inc. Other analytical grade reagents used for titration including sodium bicarbonate ($NaHCO_3$, CAS no. 144-55-8), sodium carbonate (Na_2CO_3, CAS no. 497-19-8), sodium hydroxide 0.1 mol dm^{-3} (NaOH, CAS no. 1310-73-2), and hydrochloric acid 0.1 mol dm^{-3} (HCl, CAS no. 7647-01-0) were purchased from Sigma-Aldrich Co.

The biochar provided by Pyrovac Inc. was produced by vacuum pyrolysis from a biomass feedstock composed of a 20% volume fraction of (spruce and fir) with pine (stem of Pinus strobus without bark), with a moisture mass fraction of 10%. The process conditions were a temperature of 475 °C, a pressure of 100 kPa and chips feed flow rate of 14 kg h^{-1} reaching 25% yield on a wet basis. All biochar samples used in this work were produced during the same continuous pyrolysis operation.

Physical activation was performed by placing 5 g of biochar in a vertical stainless steel tube through the middle of a furnace. Before activation, the furnace was purged with a 188 cm^3 min^{-1} nitrogen flow for 2 h, and then the temperature was raised to the desired value at the rate of 8 K min^{-1}. After reaching the desired temperature, steam was fed to the reactor, and the sample was kept under activation conditions for 60 min. After activation, the sample was cooled under nitrogen flow down to the ambient temperature. The produced activated biochar was weighed to determine the yield of reaction that is defined as the weight of final product per initial weight of the biomass before pyrolysis. The same furnace was also used for mild air oxidation. Thus, 2 g of sample was placed in the middle of the furnace and temperature was elevated to the desired value below 300 °C at the rate of 3 K min^{-1}. Then, the air was fed at a flow rate of 164 cm^3 min^{-1} into the furnace. Finally, the resultant sample was weighed again to establish the product yield.

In this study, the initial biochar, the steam-activated biochar at 900 °C during 60 min, the biochar air oxidized at 200 °C for 30 min and 60 min, and the activated biochar oxidized at 200 °C for 60 min are designated as Samples 1, 1A, 1-O-30, 1-O-60, 1A-O-60, respectively. The time and temperature of mild oxidation were selected based on preliminary tests in order to achieve a trade-off between burn-off and total acidic surface concentration (as determined by Boehm titration). The combination of a temperature of 200 °C and an air oxidation time of 60 min was found optimal.

2.2. Bulk characterization

2.2.1. Proximate analysis

Moisture and volatile matter were estimated by thermogravimetric analysis (TGA) (Q5000 SA thermogravimetric analyzer, TA Instrument Inc.). The TGA traces were recorded by placing about 5 mg–9 mg of sample inside a Pt pan; the heating rate was set to 10 K min^{-1} from 50 °C to 900 °C under 25 cm^3 min^{-1} flowing nitrogen.

In addition, the ASTM D2866–11 standard test method was applied to determine the ash content of each sample by using Isotemp® 650 series programmable muffle furnace (Fisher Scientific™, US). Concisely, five crucibles were placed in the muffle furnace at 650 °C for 1 h, cooled, weighed, and filled with 1 g of sample. Then, they were heated to 650 °C and kept for 15 h in the furnace. The mass of the remaining samples was considered as ash mass. Therefore, by considering moisture and volatile matter obtained by TGA, and ash content from the ASTM D2866–11 standard, fixed carbon was calculated by difference [3,16].

2.2.2. Elemental analysis

A TruSpec® Micro-CHN (LECO, USA) elemental analyzer of Washington State University was used to measure the total carbon (C), hydrogen (H), and nitrogen (N) contents on dry and ash free basis. The mass fraction of oxygen (O) then was obtained by difference. The oxygen to carbon atomic ratio (O/C) of the whole bulk of sample was determined from these results.

2.3. Surface physical characterization

2.3.1. Nitrogen adsorption-desorption analysis

The specific surface area and pore structure characteristic of samples were determined by nitrogen adsorption-desorption at −196 °C (Quanta Chrome NOVA 2000 instrument). As a common procedure of sample preparation, 0.05 g of each sample was placed in an adsorption cell and degassed under vacuum at 300 °C for 6 h. This time was increased to 24 h for initial and oxidized biochar with no activation since it was expected that there was no porosity in these samples. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation over the relative pressure range of 0.05–0.15. Total pore volume was found at the highest relative pressure of nitrogen adsorption (~0.99). Micropore volume and specific surface area were obtained using the Dubinin-Radushkevich (DR) and t-plot methods, respectively. Mesopore volume and surface area can be estimated by subtracting these values from the total values. The pore size distribution was obtained by using non-local density functional theory (NLDFT).

2.3.2. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The morphology of carbon samples was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) at micro and nano scales, respectively. In the SEM analysis, a small quantity of dried samples was placed in the sample container of a JSM-840A (JEOL, US) scanning electron microscope equipped with an EDX spectrometer, and sputtered with gold and palladium to acquire sufficient conductivity. A JEM-1230 (JEOL, US) transmission electron microscope was applied to investigate the surface structure at higher resolution. The TEM specimens were prepared by crushing the samples into a fine powder. Then, they were suspended in methanol for fast evaporation and higher specimen visibility along with 10 min of sonication in a sonic bath and deposited uniformly as a thin layer (200 nm or thinner thickness) on a nickel grid support followed by air drying.

2.4. Surface chemical characterization

2.4.1. Boehm titration

The concentrations of carboxyl, lactone, and phenol groups were established by using Boehm titration. For preparation of the Boehm base solution, 250 mg of each oven dried sample was added to 50 cm^3 0.1 mol dm^{-3} solutions of sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), and hydrochloric acid (HCl), respectively. All solutions were mixed for 72 h to reach equilibrium, and 10 cm^3 of those then titrated directly after filtration. HCl 0.1 mol dm^{-3} was used to titrate the first three solutions under the