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Research paper

Modification of biochar surface by air oxidation: Role of pyrolysis temperature

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ABSTRACT

This paper reports the effects of pyrolysis temperature on biochar to oxidation by air. Eighteen biochars were produced from the pyrolysis of Douglas fir wood (DFW), Douglas fir bark (DFB), and hybrid poplar wood (HP) at six temperatures (623, 673, 723, 773, 823 and 873 K) in a lab scale spoon reactor. The oxidation step for all biochars produced was conducted at 523 K in the presence of air in a spoon reactor. The elemental and proximate analyses of all the oxidized and un-oxidized chars suggest that the carbonaceous materials produced at low temperature are more susceptible to oxidation than those produced at high temperature. A number of surface properties of resultant biochars were examined to better understand how pyrolysis temperatures and feedstock sources relate to the development of surface characteristics. The removal of volatiles during the pyrolysis step resulted in the gradual creation of microporosity detectable by CO_2 adsorption but which was difficult to detect with N_2 adsorption, suggesting that the chars contain micropores mostly less than 1 nm in entrance dimension. In some cases, the surface area decreased after being oxidized likely due to the blockage of micropores by oxygen-containing functional groups. The surface composition determined by XPS and Boehm titration confirms that greater quantities of carbonyl and carboxyl groups are formed on biochars produced at low temperature. The formation of these oxygenated functional groups contributes to add negative charges on the surface and consequently the pH at the point of zero charge increases for un-oxidized biochars.

1. Introduction

The global warming caused by the release of greenhouse gases is a source of serious political concern all over the world. On this context, biomass conversion technologies are being studied for their potential to mitigate global warming. Biochar offers the potential to stabilize some of the carbon fixed by terrestrial vegetation [1–4]. While biochar has significant potential as a soil amendment, studies with freshly produced biochars have not been able to reproduce the effectiveness of the centuries old Terra Preta soils of the Amazonian Basin. One possible reason is that when the char is left in the soil for long periods of time the surface is slowly oxidized [5]. The surface oxygenated complexes (hydroxyl, carbonyl and carboxyl groups), typically at the edges of aromatic ring systems in the form of sheets are responsible for many of the physico-chemical properties of these materials [6]. These oxygenated functional groups on the surface could be to enhance their cation exchange capacity, change its surface charge and to its water holding capacity. All these properties could have an important impact enhancing soil fertility.

Surface acidic functional groups are by far the most important surface groups that not only influence the surface characteristics such as polarity, acidity, and wettability, but also physico-chemical properties such as catalytic, electrical, and chemical reactivity of carbon materials [7]. Recent studies showed that acidic groups can be formed on the surface of activated carbon in quantities of a similar order of magnitude as found in various humic materials,

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which are important degradation products of soil organic matter that contain a high proportion of carboxylic acid functional groups [6,7]. The results obtained by Valdes et al. [8], for example, indicate that total acidic groups on activated carbons (AC) can reach at least 2 meq g^{-1} with half the acidic groups in the form of carboxyls. Carboxylic acid groups are essential for improving the biochars nutrient holding capacity, as well as polarizing the surface [6,8].

Most of the biochar oxidation tests reported in the literature were conducting using aggressive reagents (ozone, hydrogen peroxide, strong acids) [6,8–12]. Although the oxidation temperature of coal and activated materials in air ranging between 393 and 523 K have been extensively studied [13–15], there are few or no published studies on the effects of pyrolysis temperature on the structure and the susceptibility of carbonaceous materials to air oxidation. The later oxidation method is of great interest to the biomass pyrolysis community because it can be easily integrated into the biochar cooling step. Thus, the main objective of this paper is to study the effect of pyrolysis temperature on the susceptibility of biochar to oxidation by air and the effect of the oxidation process on the bulk and surface properties of the resulting oxidized chars.

2. Experimental methods

2.1. Pyrolysis in spoon reactor

Three milled biomass feedstocks; woods of hybrid poplar (HP) (*Populous deltoids*) and Douglas fir (*Pseudotsuga Menziessii*) (DFW), and Douglas fir bark (DFB) were pyrolyzed at six different temperatures (623, 673, 723, 773, 823 and 873 K) using a lab-scale spoon reactor described elsewhere [16]. The Douglas fir was kindly supplied by Herman Brothers Logging in Port Angeles WA. The hybrid poplar was collected at the Boise Cascade Corporation in Pasco, WA. More information on feedstock preparation and feedstocks properties can be found elsewhere [17]. The pyrolysis experiments were conducted under an oxygen free atmosphere by purging the reactor with nitrogen (flow rate: 900 cm^3 min^{-1} at Normal Temperature and Pressure (TPN): 293.15 K and 101.3 kPa). For each run, 0.4 g of biomass was used and heating rate achieved was close to 190 K min^{-1}. The material was kept at the final temperature for 30 min. The biochar yield was calculated as a percentage of the dried feedstock left on the spoon [18,19].

2.2. Oxidation in spoon reactor

Dry air was used as an oxidizing agent (900 cm^3 min^{-1} at 293.15 K and 101.3 kPa) to modify the surface of the biochars produced. Oxidation of 0.05 g of each biochar sample was carried out in the same spoon reactor operated at 523 K for 30 min with air stream. In this paper, the biochars are denoted as HP for the hybrid poplar wood feedstock and HP-623, HP-673, HP-723, HP-773, HP-823, and HP-873 for the resulting unoxidized biochars created at the six temperatures (623, 673, 723, 773, 823, and 873 K). The oxidized samples are designated using the same abbreviation followed by capital AO, which refers to air oxidation. The same abbreviation procedure was applied for both Douglas fir wood (DFW) and Douglas fir bark (DFB) biochars.

2.3. Bulk properties

2.3.1. Elemental analysis

Elemental analysis was performed using a TRUSPEC-CHN® (LECO, US) elemental analyzer described elsewhere [17]. Briefly, 0.05 g oven dried samples were used to determine total C, N and hydrogen (H). Oxygen (O) mass fraction was determined by subtracting the ash, C, N, and H mass fraction from the total mass of the sample. These results were used to calculate atomic H/C, O/C and C/N ratios which are indicative of the bonding arrangement [20] and polarity [21].

2.3.2. Proximate analysis

Fixed carbon, volatiles, and ash mass fraction were determined by using a high temperature muffle furnace, Isotemp® (Fishe Scientific, US) and a thermo-gravimetric analyzer (TGA), SDTA851e (Mettler Toledo, US) following the methods described elsewhere [17,22–24]. Briefly, 1.5 g of oven dried samples were weighed into a pre-weighed crucible and heated in air at 848 K for 12 h in order to determine the ash mass fraction of each sample. The thermo-gravimetric method for volatiles and fixed carbon determination was performed under nitrogen atmosphere (100 cm^3 min^{-1}). Five to eight mg of each biochar sample was heated from room temperature to 378 K at a rate of 10 K min^{-1} and held at 378 K for 15 min. Next, the samples were heated from 378 to 1223 K at 30 K min^{-1} and held for 10 min.

2.4. Surface properties

2.4.1. Gas physisorption analysis

Carbon Dioxide (CO_2) adsorption isotherms were measured at and 273 K, on a Micromeritics TriStar II 3030 PLUS Surface Area and Porosity Analyzer (Norcross, GA, USA). Prior to each analysis, samples were degassed at 473 K for 18 h under a vacuum of 13.3 Pa (the degassing temperatures were chosen on the basis of TGA measurements to avoid sample degradation during preparation). CO_2 adsorption isotherms were measured in the partial pressure range $p/p^0 = 10^{-5} - 0.03$ using approximately 75 data points by a method described elsewhere [17]. The micropore volumes were estimated using the Dubinin–Radushkevich (DR) equation.

2.4.2. Cation exchange capacity (CEC)

The CEC of the samples were determined according to the method of passive barium exchanged with forced magnesium exchange described elsewhere [2,17]. Briefly, 0.4 g of each biochars in replicates was washed with 20 cm^3 of 0.1 mol dm^{-3} HCl for 1 h, and then washed with e-pure water three times. Thirty cm^3 of 0.1 mol dm^{-3} of $BaCl_2$ was added to each sample and samples were agitated for half an hour. The samples were then filtrated and mixed with 0.025 mol dm^{-3} of $BaCl_2$; pH of the mixtures was adjusted to 5.3 using $Ba(OH)_2$ or HCl. The mixtures were agitated for 24 h. After that, the $BaCl_2$ was washed out of the samples with e-pure water and then dried at 378 K. In triplicates, 0.1 g of dried samples were re-suspended in 10 cm^3 of 0.01 mol dm^{-3} $MgSO_4$ solution. After one hour of agitation, samples were filtered and the filtrates were analyzed by Atomic Adsorption, Spectra-AA220 (Varian Analytical Instruments Inc., US).

2.4.3. pH and electrical conductivity (EC)

Biochar pH and EC were determined by methods described elsewhere [25,26]. Briefly, 0.01 g cm^{-3} suspensions of biochar were prepared with deionized water, and agitated for 24 h. The biochar suspensions were then measured for both pH and EC using Hanna HI 9813-6 pH/EC/TDS meters (HANNA instruments Inc., US). The pH reading was considered stable when it did not change more than 0.1 units over 30 s. The analyses of pH and EC were performed in duplicate.

2.4.4. Zeta potential (ζ)

The zeta potential of biochar was determined using the method described by Julien et al. [17,27]. Briefly, bio-char particles were firstly ball milled in a PQ-N2 planetary ball mill (Across International LLC, NJ, USA) for 24 h to pass through a 200 mesh (opening: