



Research paper

Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties



Waled Suliman^a, James B. Harsh^a, Nehal I. Abu-Lail^b, Ann-Marie Fortuna^c,
Ian Dallmeyer^{d,e}, Manuel Garcia-Perez^{d,*}

^a Department of Crop and Soil Sciences, Washington State University, Pullman, WA, 99164, USA

^b The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, 99164, USA

^c Soil Science Department, North Dakota State University, Fargo, ND, 58108, USA

^d Biological Systems Engineering, Washington State University, Pullman, WA, 99164, USA

^e Composite Materials and Engineering Center, Washington State University, Pullman, WA, 99164, USA

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ABSTRACT

Eighteen biochar samples 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. Changes in the bulk composition of the biochar produced were examined by elemental and proximate analyses. The mass fraction of volatiles, oxygen and the ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C) decreased linearly with pyrolysis temperature. Surface properties of all the biochars produced (SEM morphology, CO₂ and N₂ adsorption, XPS analysis, Boehm titration, cation exchange capacity (CEC) and ζ-potential) were also studied. The removal of volatiles resulted in the gradual creation of microporosity detectable by CO₂ adsorption but which was difficult to detect with N₂ adsorption, suggesting that the chars contain micropores mostly less than 1 nm in entrance dimension. The XPS and Boehm titration confirmed that most oxygenated surface functional groups (presence of carbonyl, carboxyl and hydroxyl groups) are gradually removed as pyrolysis temperature increases. The changes in surface charge were studied by ζ-potential measurements and were found to vary directly with the content of oxygenated functional groups. Properties that depend on both surface area and the surface oxygenated functional groups, such as the cation exchange capacity, showed a more complex behavior. The composition of the ash and associated properties such as pH and electric conductivity (EC) were also measured. The total alkaline content increases with pyrolysis temperature leading to higher pHs and ECs.

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1. Introduction

Biochar is a carbon-rich, porous material prepared by the thermochemical reactions of organic materials in an oxygen-limited environment [1–4]. Biochar is receiving growing attention as a soil amendment due to its potential to enhance soil fertility and sequester carbon [5]. The use of biochar as a soil amendment dates back to the Amazonian Dark Earths (known as Terra Preta) in the Amazon basin where charred organic materials appear to have been added purposefully to soil to enhance its fertility [6].

A wide range of biomass feedstocks are available to manufacture biochar including wood materials, agricultural residues, forest residues and wastes from food, sugar, or juice processing [7,8]. Woody biomass is the most important source for charcoal making worldwide. Woody biomass contains varying amounts of hemicellulose, cellulose, lignin and small quantities of other organic extractives (e.g. fats, phytosterols and phenolics) and inorganic compounds (such as nitrogen, phosphorous, sulfur, silicon, alkali and alkaline earth metals, and various trace minerals). The structure of resulting biochar can vary significantly depending on botanical species, plant part, soil type, climate conditions, and the time of harvest of the feedstock used [6,9,10].

Pyrolysis is the major anaerobic thermochemical conversion method used to convert biomass into liquid fuel, gases, and charcoal [11]. The reaction mechanisms of biomass pyrolysis are

* Corresponding author. Biological Systems Engineering, WSU, LJ Smith, Room 205, Pullman, WA, 99164-6120, USA.

E-mail address: mgarcia-perez@wsu.edu (M. Garcia-Perez).

complex due to the large variation of biomass components and the large number of possible thermochemical reactions [6,12]. Slow pyrolysis is the traditional method for charcoal production, while fast pyrolysis is being actively explored for the production of renewable liquid fuels. Char is a co-product of pyrolysis regardless of the heating rate, although the relative yields of char, bio-oil, and non-condensable gases are strongly dependent on heating rate and final pyrolysis temperature [11].

The feedstock properties along with the pyrolysis temperature are the main factors affecting biochar bulk and surface characteristics [13]. Higher yield of biochar is obtained from feedstocks with high lignin and mineral content [10,14]. Likewise, carbon content of biochars can be varied by altering the raw material and/or production conditions; at high pyrolysis temperatures, woody and herbaceous biomass usually provides a more carbon-rich biochar compared to other feedstocks such as sewage sludge and animal manures [8,15]. Several studies [5,13,15–17] have reported that yield, aliphatic carbons, oxygenated functional groups, and content of nitrogen, oxygen and hydrogen in biochar decrease with increasing reaction temperature.

The function of biochar in soil is very complex. Therefore, there is a need to characterize the bulk and surface properties of biochars produced from any particular feedstock under a given set of pyrolysis conditions in detail in order to understand the properties most relevant for its use as a soil amendment [13,18]. Thus, the objectives of our research is to examine how feedstock source and pyrolysis temperature affect the bulk and surface properties of biochar. Although the information reported in this paper is relevant to many applications, the intended use of our biochars is soil amendment.

2. Materials and methods

2.1. Biochar preparation

Three different biomass feedstocks, wood hybrid poplar (*Populus deltoids*) and Douglas fir (*Pseudotsuga Menziessii*) wood and bark were studied. 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. The received chips were air-dried and ground below a 2 mm sieve size by hammer milling (model number 400 HD, serial number 2404, Bliss Industries, Inc). The resulting samples were further ball milled (Across International PQ-N2 Planetary Ball Mill) till a particle size of about 590 μm . The elemental composition of the biomass feedstocks studied is shown in Table 1.

The milled feedstocks were then pyrolyzed at six different temperatures (623, 673, 723, 773, 823 and 873 K) using a lab-scale spoon reactor described elsewhere [19]. The experiments were conducted under an oxygen free atmosphere by purging the reactor with nitrogen. For each run: heating rate and charring time were fixed at 190 K min^{-1} for 30 min, respectively. 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 biochars created at the six temperatures (623, 673, 723, 773, 823, and 873 K). The same procedure was applied to both

Douglas Fir wood (DFW) and Douglas Fir bark (DFB). The samples were thoroughly mixed with a spatula before sampling. The biochar yield (on dry basis) was calculated as a percentage of the dry feedstock input and biochar output [5,20].

2.2. Biochar characterization

2.2.1. Biochar bulk properties

2.2.1.1. Elemental analysis. Elemental analysis was performed using a TRUSPEC-CHN[®] (LECO, US) elemental analyzer. Briefly, 0.05 g oven dried samples were used to determine total carbon (C), nitrogen (N) and hydrogen (H). Oxygen (O) mass fraction was determined by subtracting the ash, C, N, and H contents 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 [21] and polarity [22].

2.2.1.2. Proximate analysis. Fixed carbon, volatiles, and ash content were determined by using a high temperature muffle furnace, Isotemp[®] (Fisher Scientific, US) and a thermogravimetric analyzer (TGA), SDTA851e (Mettler Toledo, US) following the methods described elsewhere [2,23]. 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 ash content of each sample. Moisture, volatile matter and fixed carbon were determined by TGA using Alumina 70 mm^3 crucibles. Five to 8 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. The thermogravimetric method was performed under nitrogen atmosphere (100 $\text{cm}^3 \text{min}^{-1}$) and the percentage of fixed carbon was determined by subtracting ash percentage from volatile matter percentage, after assigning all weight loss up to 423 K to loss of free and non-structural water.

2.2.1.3. Thermal recalcitrance analysis. The thermal recalcitrance of the biochar produced was studied by the thermogravimetric method described by Harvey et al. [24]. Mass loss characteristics associated with the thermal oxidation of biochars were determined using a thermogravimetric analyzer (TGA), SDTA851e (Mettler Toledo, US). In air atmosphere (air flow rate of 100 $\text{cm}^3 \text{min}^{-1}$), samples between 5 and 8 mg were heated from 298 to 378 K at 10 K min^{-1} and held at this temperature for 15 min, and then from 378 to 1223 K at 30 K min^{-1} and held for 10 min. The thermal recalcitrance index (R_{50}) of produced biochar were estimated using Equation (1) and Equation (2), respectively.

$$R_{50, \text{ biochar}} = T_{50, \text{ biochar}} / T_{50, \text{ graphite}} \quad (1)$$

Where $T_{50, \text{ biochar}}$ and $T_{50, \text{ graphite}}$ were the temperature values corresponding to 50% weight loss by oxidation/volatilization of biochar and graphite, respectively. Values for $T_{50, \text{ biochar}}$ and $T_{50, \text{ graphite}}$ were obtained from TG thermo-grams that have been corrected for water and ash content as following:

$$W_{i,c} = 100 + \left[100 * \frac{(W_{i,un} - W_{150,un})}{(W_{150,un} - W_{cutoff,un})} \right] \quad (2)$$

Where $W_{i,c}$ and $W_{i,un}$ were the corrected and uncorrected weights, respectively. $W_{150,un}$ was the weight at 423 K, and $W_{cutoff,un}$ was the weight at the temperature when no further oxidation was apparent.

Table 1
Biomass feedstock mass fraction (% dry basis).

| Feedstock | C | H | N | O ^a | Ash |
|-------------|------|-----|-----|----------------|-----|
| DF wood | 51.3 | 8.2 | 0.4 | 40.0 | 0.3 |
| DF bark | 53.4 | 7.6 | 0.8 | 35.8 | 2.4 |
| Poplar wood | 50.4 | 7.8 | 1.2 | 39.4 | 1.0 |

^a By difference.

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