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Effects of pyrolysis temperature on the hydrologically relevant porosity of willow biochar

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ABSTRACT

Biochar pore space consists of porosity of multiple length scales. In direct water holding applications like water storage for plant water uptake, the main interest is in micrometre-range porosity since these pores are able to store water that is easily available for plants. Gas adsorption measurements which are commonly used to characterize the physical pore structure of biochars are not able to quantify this pore-size range. While pyrogenetic porosity (i.e. pores formed during pyrolysis process) tends to increase with elevated process temperature, it is uncertain whether this change affects the pore space capable to store plant available water. In this study, we characterized biochar porosity with x-ray tomography which provides quantitative information on the micrometer-range porosity. We imaged willow dried at 60 °C and biochar samples pyrolysed in three different temperatures (peak temperatures 308, 384, 489 °C, heating rate 2 °C min^{-1}). Samples were carefully prepared and traced through the experiments, which allowed investigation of porosity development in micrometre size range. Pore space was quantified with image analysis of x-ray tomography images and, in addition, nanoscale porosity was examined with helium ion microscopy. The image analysis results show that initial pore structure of the raw material determines the properties of micrometre-range porosity in the studied temperature range. Thus, considering the pore-size regime relevant to the storage of plant available water, pyrolysis temperature in the studied range does not provide means to optimize the biochar structure. However, these findings do not rule out that process temperature may affect the water retention properties of biochars by modifying the chemical properties of the pore surfaces.

1. Introduction

Pyrolysis biochars are carbon-rich porous materials produced by heating biomass in the absence of oxygen. Porosity and pore size distribution of biochar depend on the raw material selection and process conditions (e.g., type of pyrolysis device, heating rate, maximum temperature and holding time at maximum temperature). Application of biochars to soils can alter and improve soil physical and chemical properties, such as hydraulic properties including hydraulic conductivity and water retention capacity (e.g. Refs. [1–3]). Biochar pore sizes can cover a wide range of scales. For direct water holding effects, the minimum pore diameter of interest is approximately 200 nm, which corresponds to the permanent wilting point with matric potential -1.5 MPa [4]. Water stored in pores smaller than this is not plant available. In addition, water stored in submicrometre pores above the permanent wilting point is not readily available for plants. For example, it has been reported that dry matter production of plants may virtually cease far before the permanent wilting point [5]. Therefore, the characterization of biochars aimed at soil amendment purposes should be focused on the micrometre-scale pores that provide water storage capacity and fast release of water to plants.

Physical characteristics of biochars are often studied by gas adsorption techniques accompanied by the Brunauer-Emmett-Teller (BET) modelling to determine the specific surface area [6] or Barrett-Joyner-Halenda (BJH) modelling to determine the pore size distribution [7]. Pore space analysis based on these methods and models is limited to

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pores smaller than 300 nm, whereby gas adsorption measurements do not tell much about the porosity in the size range that is important for biochars that are used as soil amendments to improve the water holding properties of soil [8]. In spite of this limitation, in many cases BET analysis still is the only characterization method used for physical pore space even for biochar produced for soil amendment purposes. Mercury intrusion porosimetry is able to quantify the micrometre-scale porosity of porous materials. Unfortunately the feasibility of the method is reduced by the assumptions used in interpretation of the results, which do not hold for arbitrary porous materials [9].

Numerous studies have concluded that elevated pyrolysis temperature leads to increased BET specific surface area (see, e.g., [10–15]). Microstructural evolution of biochars during carbonization was studied by Kercher and Nagle [16], who explained that the increase of specific surface area results from the creation of nanometre-range pyrogenetic pores due to the growth of high-density turbostratic crystallites. The total porosity on the other hand does not have a clear dependence on the production temperature. Gray et al. observed that total porosity remained relatively stable with increasing process temperature, which suggests that pyrogenetic nanoporosity does not have significant volume even though it can provide major part of the surface area [13].

Biochar structure is summarized in the model proposed by Gray et al. [13]. In this model the pore space of biochar consists of stable residual porosity resulting from the cellular structure of the raw material, pyrogenetic nanoporosity, and aliphatic functionality on the walls of the residual porosity. Residual pore structure is considered stable and independent of the pyrolysis temperature and forms majority of the total pore volume. Pyrogenetic nanopores are increasingly created as process temperature increases, but even at higher temperatures they form only a minor part of the total pore volume. Aliphatic functionality is volatilized at higher temperatures which results in reduced hydrophobicity.

It is thus likely that feedstock selection is of major importance when one is interested in water holding applications of biochar such as soil amendments. Cellular structure of the feedstock accounts for major part of pore volume and these pores typically are in the size range capable to store readily plant-available water. Pyrogenetic pores are increasingly created with elevated process temperature, but water in these pores is too tightly bound to be available for plants and the total volume of these pores is low. However, it is not clear if process temperature contributes to water holding also by altering the physical pore characteristics, e.g. due to shrinkage in the pore size [17], or only by changing the surface chemistry and consequently the contact angle at the pore walls [13].

Characterization of porosity development during pyrolysis is still mostly based on indirect measurements and conceptual models rather than on direct evidence. In this paper we report results of an imaging study where micrometre-scale porosity of biochars is directly imaged with x-ray computed microtomography. The three-dimensional image analysis results obtained for willow biochars pyrolysed in different temperatures are compared against gas adsorption measurements. Further information about biochar porosity is obtained with helium ion microscopy (HIM), which is a novel imaging technique within the family of scanning beam microscopes. HIM results in images with very high resolution and large field of depth, thus giving accurate information of submicrometre porosity. HIM also allows for direct imaging of non-conductive samples as the beam induced charging can be neutralized with an electron flood gun. These imaging techniques allows us to get direct evidence on the significance of process temperature on the porosity that is relevant in applications based on water holding capacity of biochar and also more generally in any application relying on the micrometre-range porosity of biochar (e.g. microbial habitats [18]). In addition, we are able to compare the importance of pore size regimes probed by gas adsorption techniques in biochar research targeting to soil amendment applications.

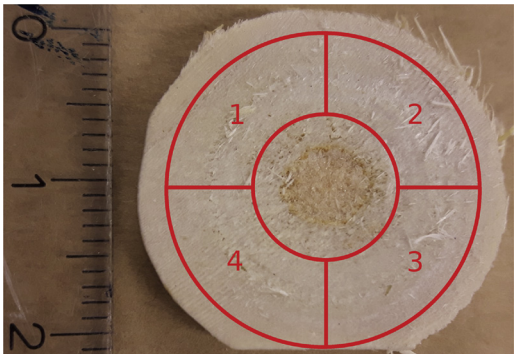

Fig. 1. Samples for imaging were prepared according to annual rings of the willow stem wood. One of the segments (1) was dried at 60 °C and three of them were in addition pyrolysed at (2) 308, (3) 384 or (4) 489 °C.

Table 1
Elemental composition, ash content, H/C and O/C atomic ratios, and BET surface area of dried and pyrolysed willow stem wood samples.

	Dried	Pyrolysed		
	60 °C	308 °C	384 °C	489 °C
C [wt-%]	44.6	67.9	75.9	83.7
H [wt-%]	5.78	4.72	4.00	3.18
N [wt-%]	0.15	0.27	0.31	0.37
S [wt-%]	0.02	0.01	0.01	0.01
O [wt-%]	48.9	25.9	18.2	8.3
H/C ratio	1.54	0.83	0.63	0.45
O/C ratio	0.82	0.29	0.18	0.07
Ash [wt-%]	0.51	1.19	1.60	4.44
BET [$m^2 g^{-1}$]	n.d.	3.96	7.47	6.82

Table 2
Results of 3D image analysis. Porosity, specific surface area (SSA), degree of anisotropy (D_A) and shape ratio S/I determined for dried willow and biochars pyrolysed at different temperatures. For S/I ratio, mean value and standard deviation were calculated separately for large and small pores.

Sample	Porosity [-]	SSA [$mm^2 mm^{-3}$]	D_A [-]	S/I (large pores) [-]	S/I (small pores) [-]
Dried willow	0.32	98	88	0.77 ± 0.12	0.77 ± 0.14
Pyrolysis at 308 °C	0.36	105	48	0.61 ± 0.20	0.63 ± 0.21
Pyrolysis at 384 °C	0.35	110	82	0.45 ± 0.15	0.61 ± 0.24
Pyrolysis at 489 °C	0.37	111	30	0.60 ± 0.14	0.62 ± 0.22

2. Materials and methods

2.1. Sample preparation

In a previous study [19] we found that pore characteristics of ostensible same biochar may vary remarkably due to the heterogeneity of the raw materials used in biochar production. In order to minimize variation in the pore space properties originating from raw material heterogenity, following sample preparation approach was used. Fresh (moisture content 54.4 ± 0.3%) willow (Salix schwerinii 'Amgunskaja') was used as raw material. The bimodal pore size distribution of willow makes it an attractive raw material for a study considering changes is pore structure. The stem wood was first peeled and then cut into thin slices with thickness ca. 5 mm and diameter ca. 2 cm. Slices were then dried at T = 60 °C for 48 h. One of the thin slices was selected for imaging (Fig. 1). The core of the samples was removed by drilling a hole (diameter 8 mm) and the part remaining was divided in 4 segments. The outermost part of each segment was also removed so that the actual samples were approximately 5 mm wide.