



Chemical modification of biomass residues during hydrothermal carbonization – What makes the difference, temperature or feedstock?

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ABSTRACT

Hydrothermal carbonization (HTC) of biomass may be a suitable technique to increase its carbon sequestration potential when applied to soils. However, the properties of end products of HTC (hydrochars) could be significantly influenced by feedstock source and temperature during the carbonization process. This study focused on chemical modification of wheat straw, poplar wood and olive residues through HTC at different temperatures (180 °C, 210 °C and 230 °C). Besides general properties such as pH, electrical conductivity (EC), ash content, elemental composition and yield, we evaluated bulk chemical composition (¹³C NMR) and contribution of specific compounds (lignin and black carbon). Moreover, the possible environmental risk of using hydrochars was assessed by determining their polycyclic aromatic hydrocarbon (PAH) and their dioxin contents. Our results showed that hydrochars were generally acidic with a pH value below 5. The highest EC (1710 μS/cm) and ash content (10.9%) were found in wheat straw derived hydrochars. Hydrochar yields and C recovery decreased with increasing temperature to about 50% and 75%, respectively for all feedstocks at 230 °C. N recovery increased with increasing temperature but N content of feedstock is more important. H/C and O/C ratios showed a linear decrease with increasing production temperature for all feedstocks. O-alkyl C decreased while alkyl C and aromatic C increased with increasing temperature and no significant feedstock dependence could be observed. Carboxyl C was not influenced by feedstock and temperature. Lignin content decreased with increasing temperature, while its oxidation degree and the content of black carbon and PAH contents increased. We conclude that transformation of biomass was most advanced at 230 °C only. Feedstock did not significantly influence the chemical composition of the hydrochars apart from N content and recovery. Instead, HTC temperature is the main driver determining the chemical composition of hydrochars. Environmental risk of investigated hydrochars is low with respect to PAH and dioxin contents. Despite the advanced biomass transformation during the HTC process at 230 °C, chemical properties indicated that the end product might have a less stable structure than pyrochar. Considering the higher hydrochar yields and C and N recoveries, its C and N sequestration potential in soil could have some advantages over hydrochars but this still remains to be evaluated.

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1. Introduction

Increase of soil carbon sequestration following biochar application to soils has been proposed as a solution to counteract rising atmospheric CO₂ concentrations and improve soil quality (Glaser et al., 2002; Marris, 2006). Usually, biochar is produced by pyrolysis of biomass (pyrochar). In recent years an alternative procedure (hydrothermal carbonization, HTC) has been developed to transform labile biomass into a more stable end product (hydrochar).

HTC is a process of heating biomass together with water at a temperature between 180 °C and 250 °C in a pressure vessel for several hours (Libra et al., 2011). Pressure cannot be controlled and depends on the steam pressure of water and gas development during feedstock decomposition. A clear scientific definition of the products of hydrothermal carbonization does not exist. From a chemical point of view, hydrochars are similar to brown coal, due to their low degree of carbonization and therewith a low degree of aromaticity and high proportion of functional groups on its surface (Libra et al., 2011; Schimmelpfennig and Glaser, 2012). The process of hydrothermal carbonization resembles a torrefaction process which involves heating at 200–300 °C at slow heating rates

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(<50 °C/min) under an anoxic atmosphere (Amonette and Joseph, 2009). Therefore, the chemical properties of hydrochars are not comparable to pyrochars because of different carbonization processes and thermochemical reactions (Cao et al., 2010). For instance, pyrochars are dominated by aromatics and hydrochars by aliphatics (Titirici et al., 2008). The chemical conversion of biomass during the HTC process is a series of hydrolysis, condensation, decarboxylation and dehydration reactions (Titirici et al., 2007; Sevilla and Fuertes, 2009a,b; Funke and Ziegler, 2010). However, knowledge about the formation of aromatic and potentially toxic compounds during hydrothermal carbonization at different temperature stages from various feedstocks is highly complex and not fully understood.

Therefore, the purpose of this study was to evaluate whether feedstock or temperature is the dominant driver for the chemical composition of hydrochars. For this purpose, nine different hydrochars were produced from three different feedstocks (poplar wood, olive residues and wheat straw) at three different temperatures (180 °C, 210 °C and 230 °C). The reactor used in this study reaches a maximum temperature of 230 °C (Section 2.2). Below a temperature of 180 °C, essentially no chemical modification of biomass occurs. Therefore, the lowest and highest possible temperatures (from a technical point of view) were chosen. The intermediate temperature of 210 °C was used for gradual traceability of the chemical conversion of biomass during the hydrothermal carbonization process.

The objectives of the present study were (i) to quantify the main influencing factors (e.g. production temperature and feedstock) regarding the chemical properties of hydrochars and (ii) to evaluate the stability of hydrochars and its contribution to long term C sequestration in soils based on its elemental and chemical composition and (iii) to evaluate the risk of hydrochars as a possible source of organic pollutants.

2. Materials and methods

2.1. Feedstocks

Chars were obtained from three different forestry and agriculture by-product feedstocks: Poplar wood chips, solid olive residues and wheat straw. Poplar (*Populus* spp. L.) wood chips, as a fast growing, renewable raw material, were obtained from dedicated short rotation forestry in northern Italy (Po Valley – Gadesco Pieve Delmona (CR), Lombardy, 45°10'13"N, 10°06'01"E). The age of the forestry at harvesting was 5 years. Solid olive residues are by-products of the olive milling process and often used as soil manure. The wet material is suitable for hydrothermal carbonization without energy intensive drying for the process as needed for pyrolysis. Olive residues were produced in Tuscany (San Giovanni Valdarno (AR), Tuscany) by means of a continuous oil extraction process with two-phase decanters. Wheat straw (*Triticum* spp. L.) was produced close to the poplar (Po Valley – Gadesco Pieve Delmona (CR), Lombardy – 45°08'59"N, 10°08'28"E) as by-product of grain and therefore available in large quantities; after harvesting, straw was chopped and briquetted. All feedstock materials were free of contaminants such as stones, metal, rubber, plastic, pollutant compounds and other foreign bodies, being direct products or by-products of agriculture.

2.2. Preparation of hydrochars

Hydrochars out of poplar wood, olive residues and wheat straw were produced at 180 °C, 210 °C and 230 °C and a corresponding average pressure of 10, 20 and 30 MPa, respectively. The producer Artec Biotechnology GmbH (Bad Königshofen, Germany) used the

reactor b.coal 2.0 for laboratory scale production. The reactor is a stainless steel autoclave, holds a volume of 1.8 l and reaches a maximum temperature of 230 °C and a maximum pressure of 40 bar (burst pressure is 55 bar). About 300 g of each type of biomass was loaded into the pressure vessel and mixed with 1000 ml water together with citric acid as catalyst. The temperature was raised to 180 °C, 210 °C or 230 °C and the reactor was kept at temperature for 8 h. After HTC, all hydrochars were separated from slurry. The solid hydrochars were dried at 40 °C in a drying oven for 48 h. Samples were ground with an oscillating disk mill.

2.3. Chemical characterization

2.3.1. pH value

For measuring pH and electrical conductivity (EC) of hydrochars and feedstocks, suspensions with 0.01 mol/l CaCl₂ and distilled H₂O (1:5) were prepared. The mixtures were shaken for 1 h on a low speed shaker at room temperature. After sedimentation of hydrochar material for another hour, EC and pH were determined in the supernatant.

2.3.2. Ash content

For determining the ash content, 0.5–2 g of sample were weighed into pre-heated (500 °C) porcelain crucibles. After 4 h drying at 105 °C in a drying oven, the samples were re-weighed after cooling in a desiccator. Ashing occurred at a temperature of 550 °C for 8 h in a muffle furnace. The temperature increase was slow (3 °C/min) to prevent the formation of open fire due to the high organic content of the samples. After cooling in a desiccator, samples were weighed again. Determination of the ash content was calculated as mass loss on an oven dry basis.

2.3.3. Elemental composition

Total C, N, S and H contents were determined at the Institute of chemistry of the Martin-Luther-University in Halle (Germany) using a “vario EL” analyser by Elementar GmbH (Hanau, Germany). The total O content was measured by using a EURO EA Elemental Analyser (EuroVector, Hekatech, Germany) at the Soil Biogeochemistry Department of the Martin-Luther-University in Halle (Germany).

2.3.4. ¹³C NMR

Solid state ¹³C NMR spectra were recorded on a Bruker DSX 200 NMR spectrometer using cross polarization magic angle spinning (CPMAS) (Schaefer and Stejskal, 1976). A spinning speed of 6.8 kHz and a contact time of 1 ms were applied. A ramped 1H pulse starting at 100% power and decreasing until 50% was used during contact time to avoid Hartmann–Hahn mismatches (Peersen et al., 1993). A pulse delay of 2 s was chosen for all samples. Spectra were integrated by the integration routing of the spectrometer after phasing and baseline correction. We chose a line broadening of 50 Hz.

2.3.5. Lignin

Lignin content of feedstock and hydrochars was analyzed after CuO oxidation (Hedges and Ertel, 1982) as modified by Kögel and Bochter (1985). Briefly, 50 mg of sample were oxidized with 250 mg CuO and 2 M NaOH at 172 °C under N₂ for 2 h. After purification of the CuO oxidation products, lignin monomers were quantified gas chromatographically after silylation with BSTFA (N,O-bis(trimethylsilyl) trifluoro-acetamide, Fluka) (Hedges and Ertel, 1982). The lignin oxidation products were separated and detected with a HP GC 6890 gas chromatograph, equipped with a SGE BPX-5 column (50 m length, 0.25 mm inner diameter, 0.32 μm coating) and a flame ionization detector. Samples were injected in split mode (1:10). The GC oven temperature was programmed

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