



# Effects of selected process conditions on the stability of hydrochar in low-carbon sandy soil



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## ABSTRACT

Biochars have been found to enhance soil properties and to reduce atmospheric greenhouse gases due to their stable carbon fractions. It is known that stable carbon fractions of pyrolysis-derived biochars usually exhibit mean residence times (MRTs) of at least several hundred years. However, only a few studies exist on the stability of hydrochars, which are produced by hydrothermal carbonization (HTC).

This study examined the influence of two feedstock materials, straw digestate and poplar, and several processing and treatment parameters (carbonization temperature, washing of hydrochars and recirculating of process water) on the stability of hydrochars in a carbon-poor sandy soil. The results show that HTC leads to a product of variable carbon fractions with different stabilities as reflected in the different rates of CO<sub>2</sub>-C release from soil incubations within the first weeks. The carbon pool of the hydrochars could be classified into a readily available and a fast-cycling decade-scale fraction. No slow-cycling centennial-scale carbon fraction was observed in this 120-day study.

Moreover, a high reaction temperature and enhanced recirculation rate of process liquor lead to higher stability of the hydrochars. Based on the two-pool model, the more stable carbon had an MRT of 4–15 years depending on the reaction temperature and an MRT of 11–14 years for the recirculation of process liquor. The main hypothesis, that this short-term study of 120 days allows a reliable description of the long-term degradability of hydrochars, could not be confirmed.

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## 1. Introduction

Biogas is recognized worldwide as a highly valuable renewable energy and it is produced and used extensively. In the ongoing search for new types of suitable feedstock, agricultural wastes and by-products such as manure and straw are receiving more attention (Chen et al., 2014; Ribeiro and Raiher, 2013). However, the increased desire to put agricultural waste biomass to more complete use is not due to the demand for biogas production alone, but can be ascribed to the prosperous bio-based economy in general. On the one hand this can be a boon to the local economy, since new applications and higher prices for organic wastes add value to agricultural production and provide new business opportunities. On the other hand, higher withdrawal of biomass from the field can interfere with the soil's carbon balance and consequently threaten soil fertility (Thornley et al., 2014). A possible solution to this conflict of

interest could be to stabilize organic wastes prior to their soil use, so that much less carbon needs to be returned. One of the options for stabilizing biomass is to convert it to biochar by pyrolysis. This has attracted considerable attention as a possible solution for both sequestering atmospheric carbon and simultaneously enhancing soil properties (Lehmann, 2007). Despite the large diversity in experimental results, pyrogenic carbon is assumed to have a high MRT, with turnover on a centennial scale (Singh et al., 2012a). While pyrolysis is by far the most commonly used technology to produce biochar, in recent years interest has expanded to the HTC process, especially for organic waste treatment (Titirici et al., 2007). The use of HTC, which is a water-based process, can eliminate the energy-intensive drying step for wet feedstocks. One abundant type of water-rich biomass is the residue emerging from the biogas production unit after anaerobic digestion, called digestate. Digestate has been reported to contain 44.3–98.5% water, while its dry matter is largely organic (38.6–75.4%) (Nkoa, 2014).

However, the solid products of HTC and dry pyrolysis do not have the same chemical composition due to the different reaction mechanisms that lead to carbonization (Falco et al., 2011b; Libra et al., 2011). Therefore, it is important to differentiate between the two chars in terminology and in studies of potential applications. The term 'pyrochar' is used here to denote char produced by dry pyrolysis, whereas hydrothermally

*Abbreviations:* DAF, dry and ash free; DM, dry matter; FM, fresh matter; HTC, hydrothermal carbonization; LSM, least square method; MRT, mean residence time; ODM, organic dry matter; P, poplar; rec, recycled; Sd, straw digestate; SOM, soil organic matter; unw, unwashed; VDLUFA, Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten e.V.; w, washed.

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produced char is called 'hydrochar' (Libra et al., 2011). The authors point out that this terminology is irrespective of the chemical nature of the product and that a fraction of the hydrochar rather resembles 'coke' as defined by Fitzer et al. (1995); Antal and Grønli (2003) and Kruse et al. (2013). Indeed, the chars themselves may contain very heterogeneous structures or pools of carbon. As a consequence of this difference in chemical nature, there is still an urgent need to investigate whether the concepts proposed for pyrochar will also work with hydrochar. Since this paper deals exclusively with the stability of hydrochar, the dry poplar wood chips were also carbonized by HTC and not by pyrolysis for the purpose of comparison with the hydrochars produced from the wet feedstock straw digestate.

HTC is a well-known process for converting biomass to a product comparable with lignite. It has been used as a laboratory simulation method for natural coalification for decades and is often termed hydrous pyrolysis (Krevelen, 1993; Wilkins and George, 2002). Practical applications of this conversion process existed to a limited extent for dewatering of lignite (Fohl et al., 1987) and peat beneficiation (Mensingher, 1980). Recently, HTC has been increasingly used for the production of carbonaceous nanocomposites and functionalized porous materials (Titirici et al., 2012; Wang et al., 2001). However, little is known about using the solid product from HTC in soils (Dicke et al., 2014; Eibisch et al., 2015; Libra et al., 2011). A strong influence of HTC reaction temperature on the MRT in soil has already been described (Gajić et al., 2012), but in general the stability of hydrochars in soil is lower than that of pyrochars (Bamminger et al., 2014; Steinbeiss et al., 2009).

The overall aim of this work is to determine to what extent HTC process conditions and post-treatments influence the stability of hydrochar in a carbon-poor sandy soil. It is hypothesized, that the lignin content of the biomass can be used as an indicator for the stability of hydrochars. The main hypothesis is that the long-term degradability of hydrochars can be described by fractionating the carbon pool in terms of biodegradability within this 120-day study.

## 2. Materials and methods

### 2.1. Materials

For this study, a carbon-poor soil with 0.62% carbon (corresponding to 1.3% DM soil organic matter (SOM)), a C/N ratio of 10.9 and a pH of 7.2 was used. The solum (0–30 cm), taken at Leibniz-Institute of Vegetable and Ornamental Crops (IGZ) in Grossbeeren (Germany), south of Berlin, was determined as a pure sand (1.3% clay, 7.9% silt and 90.8% sand) according to DIN ISO 11277:2002-08 (2002). It represents a Cambisol, which is often found in Northeast Germany.

Two different kinds of biomass were used for the production of hydrochar: straw digestate (Sd) and poplar wood chips (P) (Table 1). The wet straw digestate was obtained from an upflow anaerobic solid-state reactor (Mumme et al., 2010) as residue of biomethane production at 55 °C (Pohl et al., 2012). Poplar wood was provided by the Saxon State Office for Environment, Agriculture and Geology (Germany). The hybrid

**Table 1**  
Characterization of feedstock.

Parameter	Straw digestate		Poplar		Unit
Cellulose	46.1	±1.4	48.8	±4.5	%DM
Hemicellulose	26.1	±0.3	15.5	±1.4	%DM
Lignin	15.6	±0.3	21.3	±4.4	%DM
DM <sup>a</sup>	14.7		95.2		%FM <sup>c</sup>
ODM <sup>b</sup>	94.0		97.7		%DM
Volatile matter	72.6	±1.2	79.2		%

The value after a plus-or-minus sign indicates the standard deviation of multiple analyses.

<sup>a</sup> Dry matter.

<sup>b</sup> Organic dry matter.

<sup>c</sup> Fresh matter.

poplars grew four to five years in a short-rotation coppice (N51°30' 7.25", E13°7'20.28") up to February 2012. The wood from a mixture of several poplar trees was cut into chips with a length of 2 mm (Pulverisette 19, Fritsch) and dried for 24 h at 105 °C. Further information is given in Table 1.

### 2.2. Hydrochar sample preparation

Hydrochars were produced using a 1 L General Purpose Bench Top Reactor (Series 4520 from Parr). The amounts of feedstocks in the respective production runs were 48 g of dried poplar wood chips (105 °C) or 300 g of fresh wet digestate. In order to achieve a dry matter content of 10%, the reactor was filled each time with deionized water to reach a total mass of 480 g. Poplar was carbonized at 230 °C. For straw digestate, the reactor was heated to three different temperatures (210 °C, 230 °C and 250 °C) using a constant heating rate of 1.7 K min<sup>-1</sup>. The temperatures were maintained for six hours in each case.

All char samples were prepared in triplicate, except for the runs at 230 °C to study the effect of recirculating the process liquor. In this case, six hydrochars were produced at 230 °C, and the process liquor from the previous run was recirculated. To study the last parameter, hydrochar samples with and without post-process washing were produced. The hydrochars were washed by adding 100 mL of deionized water to the filter cake six times. Before further use all the hydrochars were dried at 105 °C for at least 15 h.

### 2.3. Determination of the carbon balance of the HTC-process

From each run, solid hydrochar, process water and gas were collected, balanced and analyzed. To determine the carbon balance from the HTC-process, gas was collected in a bag and its volume was determined by using an eudiometer. The amounts of CO<sub>2</sub> and CH<sub>4</sub> were determined using the gas measuring equipment "Geotech GA2000" (Geotechnical Instruments).

Carbon partitioning between the phases was calculated using the following equations. The amount of carbon in g C was determined for the biomass and hydrochars using Eq. (1). Here,  $m_{\text{solids}}$  denotes the mass of biomass or hydrochar in g DM and  $x(\text{carbon})_{\text{solids}}$  denotes the measured percentage of carbon on a mass basis.

$$m(\text{carbon})_{\text{solids}} = m_{\text{solids}} * x(\text{carbon})_{\text{solids}} / 100 \quad (1)$$

The amount of carbon (in g C) in process liquor or washing water was calculated as follows:

$$m(\text{carbon})_{\text{liquids}} = m_{\text{liquids}} * \text{TOC} / \rho \quad (2)$$

Here,  $m_{\text{liquids}}$  denotes the mass of process liquor or washing water in g, and TOC denotes its measured total organic carbon.  $\rho$  is the density of process liquor or washing water. The calculation of carbon in the gas was carried out as follows:

$$m(\text{carbon})_{\text{gas}} = V * M(\text{C}) * (x(\text{CO}_2)_{\text{Gas}} * \rho(\text{CO}_2)_{\text{Gas}} / M(\text{CO}_2)_{\text{Gas}} + x(\text{CH}_4)_{\text{Gas}} * \rho(\text{CH}_4)_{\text{Gas}} / M(\text{CH}_4)_{\text{Gas}}) / 100. \quad (3)$$

The  $x$  describes the measured amounts of CO<sub>2</sub> or CH<sub>4</sub> in % on a volume basis,  $M$  is the molecular mass for C, CO<sub>2</sub> or CH<sub>4</sub>,  $\rho$  is the density of CO<sub>2</sub> or CH<sub>4</sub>, and  $V$  denotes the measured gas volume. Subsequently, the percentage distribution of carbon was determined.

### 2.4. Chemical analyses

The pH-value of soil and hydrochar was determined according to VDLUFA I A 5.1.1 (Methodenbuch Band I, 1991 comparable to DIN ISO 10390:2005-12, 2005), and for biomasses DIN 38404-5:2009-07 (2009)

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