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Chemical and morphological changes in hydrochars derived from microcrystalline cellulose and investigated by chromatographic, spectroscopic and adsorption techniques

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HIGHLIGHTS

- Hydrochars from MCC are characterized by a multi method approach.
- Between 230–270 °C and 2–10 h, the carbon content changes were very weak.
- FT-IR and NMR yield detailed information on the functional groups in hydrochars.
- Surface area and pore volume was highest at 230 °C, and aromaticity at 270 °C.

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ABSTRACT

Hydrothermal carbonization (HTC) can be used for converting the biomass into a carbon-rich material, whose application as a fuel requires higher heating value, whereas soil amendment needs stable carbon. This work was focused on the characterization of hydrochars derived from microcrystalline cellulose. The chars were investigated using elemental analysis, Brunauer–Emmett–Teller technique, nuclear magnetic resonance spectroscopy, Raman, Fourier transform infrared, and electron spin resonance spectroscopy. Severity in temperature between 230 and 270 °C with reaction times between 2 and 10 h only affect the carbon content moderately. The results show that aromatization of HTC chars correlates well with temperature, which was further supported by the increase of organic radicals with decreasing g values at higher temperatures. Based on these results, the energetic use of chars favors mild HTC ($T < 230$ °C and $t \leqslant 6$ h), while the soil amendement favors serve conditions ($T \geqslant 230$ °C, and $t > 6$ h).

1. Introduction

In the case of global warming, pyrolysed biomass, well-known as biochar, is vividly discussed as an option to remedy the CO_2 accumulation in the atmosphere. Furthermore, the production of biochar is considered as a promising way to valorize various organic wastes, such as municipal, industrial, agricultural, and forestry waste. Besides the beneficiation of climate change, biochar offers other potential applications including soil improvement (Lehmann and Joseph, 2009), chemical filter for the degradation of organic pollutants (Weiner et al., 2013), and alternative solid fuel (Reza et al., 2013). However, the practical implementation of biochar is still questioned for its economic viability and possible toxic effects for the environment (Reddy, 2010). Whereas conventional gasification, pyrolysis, and torrefaction are established thermochemical methods for biomass valorization, HTC is a relative new process. The specific advantage of HTC over the other thermochemical treatments, is the ability to use wet feedstocks. However, the process takes place under high pressure (2–5 MPa), which can be a limiting factor in plant design and system efficiency. HTC is a method for thermochemical treatment of various organic wastes for producing chars, which may be defined as hydrochars. The physical and chemical characteristics of hydrochars differ for a wide range of applications such as soil application, energy purpose, sorption of toxic compounds, purification, and catalysis (Goto et al., 2004; Wang et al., 2011).

For soil application, hydrochars are considered to improve soil quality, to increase crop yields, and to sequestrate carbon (Goto et al., 2004; Reddy, 2010). Hence, for soil application, hydrochar must be designed specially with distinct physical and chemical properties such as high surface area, low bulk density, neutral pH

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(for improving sorption capacity of nutrients), high aromaticity (as an indicator of the carbon stability in soil), and absence of toxic compounds. These stated properties are greatly influenced by both the feedstock as well as process conditions (Day et al., 2005; Sevilla and Fuertes, 2009). Recently, Becker et al. (2013), showed that the amount of volatile organic compounds (VOCs) in hydrochar can be correlated with the phenolic compounds and the process temperature. In fact, the amount of VOCs and phenolic compounds increases proportionally with process temperature, which is also known as phytotoxic effect. Meanwhile, the degree of condensation in carbonaceous material depends on the temperature and reaction time of the thermal treatment. Therefore, the optimal process conditions must be identified, where the physical and chemical properties of hydrochars are ideal for the application in soils along with lower VOC content.

The mechanism of HTC includes the dehydration of the carbohydrate into furan-like molecules (furfural aldehyde and/or 5-(hydroxymethyl)-2-furaldehyde), subsequent polymerization (condensation), and decarbonization (Sevilla and Fuertes, 2009; Titirici et al., 2008). Input materials and process conditions affect the chemical properties of hydrochars such as elemental composition (Mumme et al., 2011; Sevilla and Fuertes, 2009). This also applies to the physical parameter such as specific surface area, specific pore volume, and pore size distribution. For potential applications like chemical absorbent, and/or soil improvement, the specific surface area of hydrochar is an important physical property, which is affected by the process conditions such as temperature and pH (Sevilla and Fuertes, 2009; Mumme et al., 2011). The pore volume can be divided into macro-and micro-pores. For example, micropores contribute most to the surface area of biochar and to a higher adsorptive capacities (Rouquerol et al., 1999), while macropores may provide a suitable habitat for microorganisms in the soil (Lehmann and Joseph, 2009).

The hydrothermal treatment of biomass has been described by various authors. For process engineering, the chemical mechanism of the HTC has been investigated by Funke and Ziegler (2010), and the reaction kinetics by Reza et al. (2013). Stemann gives an overview of the characteristic properties of the resulting liquid phase during the hydrothermal carbonization of lignocellulosic biomass in Stemann et al. (2013). A comparative review of the wet (HTC) and dry pyrolysis was given by Libra et al. (2011). From the viewpoint of process engineering, energy efficiency and product quality require sufficient insight of the thermochemical conversion process as they are a prerequisite for effective reactor and process design. The emphasis of this work was therefore answer the question, to which extent temperature, pH, and time influence on the physicochemical properties of hydrochar, and how these changes can be characterized efficiently.

For this purpose, the physico-chemical properties of different hydrochars derived from cellulose were studied under the variation of process temperature, initial pH, and reaction time based on a Box–Behnken partial factorial design. Cellulose is one of the major constituents of all types of natural organic matter used in hydrochar production. Therefore, and because of the high homogeneity of the material, cellulose derived hydrochars were prepared as a model compound. Special emphasis was placed on the char's elemental composition, such as carbon, hydrogen, nitrogen, and sulphur (CHNS), the final pH of the char-liquor-suspension, and Brunauer, Emmett, and Teller (BET) surface area. In addition, selected samples were characterized by nuclear magnetic resonance (NMR), electron spin resonance (ESR), Fourier-transformed infrared (FTIR), and Raman spectroscopy to identify changes on a molecular level. Based on the spectroscopic data, furthermore, a comparison to previous studies is possible as those methods are widely used to identify the molecular structures of various products in biochar production (Ingram et al., 1954; Titirici et al., 2011).

2. Methods

2.1. Experimental procedure

The industrial microcrystalline cellulose (MCC), Avicel PH 101 (Sigma–Aldrich, Switzerland), was used as the sole feedstock in this study. Avicel PH 101 is a microcrystalline, powdery material with an average particle size of 50 μm and a bulk density of 0.28 g/cm^3. The experiments were carried out in a 1 L stirred pressure reactor using distilled water as a process medium. The reactor's initial dry matter concentration of Avicel was 97 g/L. Process temperatures were 190, 230, and 270 °C, while reaction times were 2, 6, and 10 h and pH values maintained at 3, 5, and 7, by applying citric acid. The working pressure range was between 1.7 MPa (at 190 °C) and 2.9 MPa (at 270 °C). The statistical software "Design Expert" was used to plan and evaluate the experimental work, using a Box–Behnken partial factorial design. This reduced the number of trials from 27 (3^3) to 15.

2.2. Characterization of physicochemical properties

The specific surface area was determined based on nitrogen adsorption and the BET method. The sample CE-10 (at 190 °C) hat to be carefully pestled to enable filling into sample cells. The samples were degassed under vacuum at 20 °C until pressure increase was ⩽10 micron per minute. This required degassing time of hydrochars between 53–72 (sample CE-10), 39–49 (sample CE-09), and 19–33 h (sample CE-12). All surface and porosity analyses were made with a Autosorb-1 (Quantachrome) using nitrogen as adsorbate. The adsorption and desorption isotherms were evaluated a 77 K. In the relative pressure range P/P_0 of 0.05–0.3 the specific surface area of the chars was quantified with the BET adsorption method (use of BET equation ISO 9277). Micropores were determined by Dubinin–Radushkevich (DR) adsorption method (DIN 66135-3) in a relative pressure range of 0.00,004–0.08. The analysis of mesopores was determined in a relative pressure range of 0.99–0.3 according to Barrett, Joyner and Halenda (BJH) desorption method (DIN 66134).

To investigate the influence of the process setting on the hydrochars' microscopic structure, the surface morphology of the hydrochars was studied using the Hitachi scanning electron microscope (SEM) S-2700. The dried (105 °C) sample material was mounted on the sample holder and sputtered with about 25 nm of gold (to avoid electrical charging of samples). The SEM images were made at the ZELMI at the technical university to Berlin.

2.2.1. The ultimate analysis

The ultimate analysis was obtained by using carbon, hydrogen, nitrogen, and sulphur (CHNS) analyzer (Elementar Analysensysteme Hanau, Germany). Each sample was analyzed three times, and the oxygen composition calculated by the difference method (O% = 100 − (C% + H% + N% + S%)). Dry matter (DM) was determined by treating feedstock at 105 °C for 24 h and the heat of combustion was calculated using the correlation of Boie (1953). The gel-based probe SenTix41 (WTW, Weilheim, Germany) was used to determine the pH of the liquid phase, and a Fisons GC-FID 8000 from Thermo Fischer Scientific (Italy), equipped with a PERMABOND FFAP capillary column to determine the concentration of volatile fatty acids.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

Spectroscopic characterization was in general performed on powdered, dry samples processed over 6 h at pH 5 without any further treatment. *Solid state ^{13}C cross polarization magic angle spinning*