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Effects of pyrolysis conditions on *Miscanthus* and corncob chars: Characterization by IR, solid state NMR and BPCA analysis

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ABSTRACT

Infrared and ^{13}C solid state nuclear magnetic resonance spectroscopies and benzene polycarboxylic acids (BPCA) analysis were used to characterize the structural changes occurring during slow pyrolysis of corncob and *Miscanthus* at different temperatures from 235 °C to 800 °C. In the case of corncob, a char sample obtained from flash carbonization was also investigated. Spectroscopic techniques gave detailed information on the transformations of the different biomass components, whereas BPCA analysis allowed the amount of aromatic structures present in the different chars and the degree of aromatic condensation to be determined. The results showed that above 500 °C both corncob and *Miscanthus* give polyaromatic solid residues with similar degree of aromatic condensation but with differences in the structure. On the other hand, at lower temperatures, char composition was observed to depend on the different cellulose/hemicellulose/lignin ratios in the feedstocks. Flash carbonization was found to mainly affect the degree of aromatic condensation.

1. Introduction

Biomass is a valuable resource that is receiving growing attention thanks to its great potential in relation to renewable energy production and environmental issues. Biomass is currently utilized in thermochemical processes for the production of biofuels; in this process char is also produced, which can be considered as highly valuable "green" carbon. The conversion of biomass into char to be used as soil amendment represents *per se* an efficient carbon sequestration method while at the same time improving soil fertility [1]. Biomass-derived char can also be combusted for heat and power or used for applications in several crucial fields, such as water purification, catalysis, electronics, and biomedicine [2,3].

Different technologies can be used to produce carbonized organic matter, i.e. slow and fast pyrolysis, gasification, hydrothermal carbonization, and flash carbonization [3,4]. The pyrolysis treatment induces successive chemical reactions of biomass with increasing temperature, i.e. dehydration, decarboxylation, and polymerization, which cause a progressive loss of hydrogen and oxygen and a related enrichment in carbon, with an increase in aromatic groups and eventually the condensation into aromatic clusters. In particular, two different aromatic phases are typically distinguished, i.e. an amorphous phase with randomly organized aromatic rings and a crystalline phase constituted by polyaromatic sheets [5]. These molecular scale alterations also cause changes in bulk properties, such as surface area, cation exchange capacity, electrical conductivity, magnetic susceptibility, and crystallinity [6].

The structure of char produced by pyrolysis strongly depends on process parameters, such as energy supply rate, highest treatment temperature (HTT) reached, pressure, and carrier gas composition [7]. HTT in particular has great influence on the chemical nature of chars, which may vary from slightly charred biomass, when produced at temperatures as low as 200 °C, to highly aromatic chars at temperatures up to 800 °C and beyond [8]. Thus, the potential applications of the resulting char can be quite different, depending on the chemical and physical properties of the feedstock, the method, and the treatment conditions used. For example, the production temperature determines the surface properties of chars (e.g. surface area, pH and cation exchange capacity) [9], relevant for the use of char as soil conditioner, as well as the aromaticity and degree of aromatic condensation, which

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determine the stability of char against degradation in the environment [10], with implications for the carbon cycle [11]. Hence, a detailed knowledge of the structure of char is important for its use in soils. Due to the growing concern for climate change and the need to mitigate greenhouse gases, several research groups have recently responded to the challenge of understanding the relationship between the properties of chars obtained from biomass and the process conditions used to produce them [12]. To this end, different instrumental techniques and analytical methods have been applied in order to obtain a more thorough physico-chemical characterization of chars, as, for example, ^{13}C solid state Nuclear Magnetic Resonance (SS-NMR) spectroscopy [13] and NMR relaxometry [14], pyrolysis-GC/MS [15], and benzene polycarboxylic acids (BPCA) analysis [16].

The overall purpose of this study was to characterize the structure of chars obtained from two different biomass materials, i.e. *Miscanthus* and corncob, produced by slow pyrolysis with different HTT values and, in the case of corncob, also by flash carbonization. Both types of biomass examined have great potential for useful char production: *Miscanthus* is a high-yielding crop requiring minimal soil preparation, while corncob is an agricultural residue. Infrared (IR) and ^{13}C SS-NMR spectroscopies, two valuable complementary methods for a qualitative and quantitative investigation of the functional groups present in chars, were used. In particular, ^{13}C SS-NMR allows the aromatization degree as well as the size of the aromatic clusters to be estimated [17–22]. Information on the degree of aromatic condensation was also obtained from elemental [23] and BPCA [22,24,25] analyses, the latter allowing the relative contribution of individual molecular markers that reflect the size of the aromatic clusters to be assessed. The combined application of these techniques to the different char samples gave clear indication on the reactions that take place during pyrolysis of corncob and *Miscanthus* and highlighted structural differences between chars obtained from the two biomass materials under the same process conditions.

2. Materials and methods

2.1. Samples

Feedstocks and biochars from a previous study [9] were used. Two carbonization methods were considered, i.e. slow pyrolysis and flash carbonization. Slow pyrolysis was applied to chaffed biomass of grass (*Miscanthus giganteus*) and corncob from maize (*Zea mays*) grown in Serbia (ZP Maize Hybrid 505); flash carbonization was performed on a batch of corncobs from Waimanalo Farm in Hawaii.

In the case of slow pyrolysis the feedstock was prepared as described elsewhere [9]. Target temperatures ranged from 250 to 800 °C and the heating rate was 2.5 °C min^{-1}. Heat supply from the furnace was stopped upon attainment of the set temperature, and the sample was allowed to cool slowly to room temperature. Since exothermic reactions occurred between 250 and 400 °C, the HTT values, resulting from the average of the four thermocouples, were actually higher than the set temperatures.

Flash carbonization was performed according to the method of Antal et al. [26]. The reaction was carried out at 600 °C and lasted 20 min in a vessel pressurized with air, as described in detail elsewhere [9].

All samples were crushed through a 2 mm sieve, ground for greater homogeneity with a ball mill for 3 min at 20 s^{-1} shaking frequency (MM 200, Retsch GmbH, Haan, Germany), and then stored in airtight bags.

2.2. Infrared reflectance spectroscopy

Mid-infrared spectra were recorded using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific Inc., Madison, WI, USA) using diamond attenuated total reflectance (ATR) spectroscopy. Before analysis, each sample was finely ground for two minutes using an agate mortar and then dried at 105 °C to avoid unsystematic influence of possible residual water. After drying, the samples were placed in a desiccator until analysis. 50 mg sample was transferred to the sample holder plate and gently compressed with a spatula to achieve a smooth surface. All samples were analysed in 5 replicates over the spectral range 4000–600 cm^{-1}, with spectral resolution of 4 cm^{-1} and 32 scans per replicate. For the samples produced at the highest temperatures 64 scans per replicate were used.

After baseline correction, performed by Global Parametric Time Warping in R within the PTW package [27,28], the spectra were analysed by deconvolution of the following regions: the saturated (SAT) region from 2980 to 2820 cm^{-1} corresponding to the aliphatic C—H stretching vibration; the unsaturated region from 1800 to 1525 cm^{-1} corresponding to C=O and aromatic C=C bonds; the polysaccharide region from 1185 to 915 cm^{-1} corresponding to O-Alkyl C; the aromatic CH (aroCH) region from 855 to 740 cm^{-1}. The unsaturated region was further divided into the contributions from C=O (1800–1700 cm^{-1}) and from C=C (1650–1525 cm^{-1}). The signal integrals were used to calculate the aromaticity index $AI_{MIR} = I_{C=C}/I_{SAT}$ [29].

2.3. ^{13}C SS-NMR spectroscopy

^{13}C magic angle spinning (MAS) NMR spectra were recorded on a Bruker AMX300WB spectrometer operating at 300.13 MHz for proton and 75.47 MHz for carbon-13, equipped with a 4 mm CP-MAS probehead. Both the ^{1}H and ^{13}C 90° pulses were 3.5 µs. Direct excitation (DE) ^{13}C spectra were recorded with proton dipolar decoupling with a recycle delay of 30 s. ^{1}H–^{13}C cross-polarization (CP) spectra with proton dipolar decoupling were recorded using a contact time of 2 ms and a recycle delay of 6 s. The RF field strength was 71.5 kHz both for CP and for dipolar decoupling. The experimental parameters were optimized after preliminary tests in order to obtain a higher overall S/N ratio. All spectra were recorded at room temperature with a MAS rate of 8 kHz; in all cases 4000 scans were acquired. The chemical shifts were referenced to TMS using adamantane as external standard. Deconvolution of the spectra was performed using the SPORT-NMR software [30]. The relative signal intensities were used to estimate the contribution of the different functional groups and components, following the procedure described by Preston et al. [31]. The degree of aromaticity was estimated from the relative signal intensity of aromatic carbons ($AI_{NMR} = I_{aromatic\ C}/I_{total\ C}$) in DE-MAS spectra.

2.4. Electron paramagnetic resonance (EPR) spectroscopy

EPR measurements were performed using a Varian (Palo Alto, CA) E112 X-band spectrometer. Spectra were recorded at room temperature using a standard EPR cavity, a microwave power of 1 mW, a time constant of 0.125 s, and a modulation amplitude of 1.25 G. Feedstock and char powders (~20 mg) were inserted in quartz tubes with an internal diameter of 3 mm. Quantification of organic radicals was performed by comparing the double integral of the signal with that of the standard Varian strong pitch measured under identical instrumental conditions [32].

2.5. BPCA analysis

The method of Wiedemeier et al. [16] was applied to milled char and feedstock (Retsch MM301) weighed into quartz tubes in triplicates of 10, 15, and 20 mg. In brief, the samples were digested with 2 mL of 65% HNO_3 for 8 h at 170 °C using sealed pressure chambers (Seif Aufschlusstechnik). The digestates were filtered through ashless grade filter paper (Whatman 589/3) and washed with Millipore water, stopping further digestion by dilution. Aliquots of the resulting samples were passed through cation exchange resin and freeze-dried after