Hydrothermal carbonization of biomass as a route for the sequestration of CO₂: Chemical and structural properties of the carbonized products

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Abstract

A highly functionalized carbonaceous material (hydrochar) was obtained by means of the hydrothermal carbonization (250 °C) of two representative types of biomass, i. e. eucalyptus sawdust and barley straw. This product has a brown colour, it contains around 50-60 % of the carbon present in the biomass and it is composed by particles that retain the cellular appearance of the raw material. These particles are covered by microspheres (1-10 microns) which probably have been produced as consequence of the transformation of the cellulosic fraction. From a chemical point of view, the hydrochar products have a high degree of aromatization and they contain a large amount of oxygen-containing groups (i. e. carbonyl, carboxylic, hydroxyl, quinone, ester, etc) as deduced from Raman, IR and XPS spectroscopic techniques. The presence of these oxygen functionalities at the surface of hydrochar particles determines its high water affinity (hydrophilic properties). On the basis of the highly condensed chemical nature of the hydrochar products, we postulated that this material has a recalcitrant nature that could lead to a significant increase in carbon turnover time in relation to the biomass. This suggests an important route for the sequestration of CO₂ present in the atmosphere.

1. Introduction

The pyrolysis of biomass at low-temperatures (400-600°C) at slow heating rates is a well known procedure for obtaining a carbon-rich solid (C~ 80-90 wt %) commonly referred to as charcoal. This material is now generating great interest within the context of global climate change. In a pioneering dissertation in 1993, Seifritz suggested that anthropogenic CO₂ emissions could be mitigated by converting biomass into charcoal [1]. Indeed, the conversion of biomass (short-term biodegradable carbon) into a more durable form of carbon (charcoal) could provide a way to remove CO₂ from the atmosphere, thereby compensating for the effect of anthropogenic CO₂ emissions. The charcoal produced for this purpose is commonly denoted as biochar. The use of the biochar strategy for CO₂ mitigation has attracted huge interest in recent years [2e5]. An analysis of the process for the conversion of biomass into biochar reveals two drawbacks. Firstly, the pyrolysis of biomass generates harmful gases (CO, CH₄, C₂-hydrocarbons and polycyclic aromatic hydrocarbons) and oils [6,7]. The release of these products to the atmosphere must to be avoided and they must be recovered in order to produce energy (bioenergy). However control over the emissions of these substances, their recovery and management involves the use of complex pyrolysis equipment, which is considerably more sophisticated and costly than the traditional kilns. The other drawback is that the biochar powders obtained, must first be stored in large piles, which entails the risk of autoignition due to aerial oxidation.

It is important to explore other alternatives, besides the biochar route, for the conversion of biomass into a carbonized material with a high resistance to biochemical degradation. The hydrothermal carbonization of biomass may be one such alternative. Recently, Titirici et al. discussed the possibility of applying this process for the sequestration of atmospheric CO₂ [8]. These authors applied this synthesis strategy to

several types of saccharides in order to prepare a variety of functional porous carbonaceous materials [9]. We investigated the mechanism of hydrothermal carbonization of simple saccharides (glucose, sucrose and starch) [10] and cellulose [11] and employed the resulting carbonaceous products as a platform for the synthesis of graphitic carbon nanostructures [12]. In the Supplementary Information section we analyze and compare the biochar and hydrochar routes for the conversion of biomass into recalcitrant forms of carbon.

The hydrothermal carbonization of biomass involves treating this material, mixed with a certain amount of water, in an autoclave, at a temperature of around 250 °C (generated pressure $\sim$ 4 MPa) for a period of 2-6 h. The resulting products consist of: a) an aqueous solution containing furfural-like products and b) a carbon-rich solid denoted here as hydrochar. Our hypothesis is that hydrochar may constitute another reliable option (besides biochar) for CO₂ biosequestration. Preliminary studies carried out in our laboratory suggest that the carbon contained in the hydrochar has a recalcitrant nature (i.e. long-term mineralization) [13]. Like biochar, hydrochar can also be produced at a global level from a large variety of biomass sources. However, unlike pyrolysis, hydrothermal carbonization does not generate large amounts of harmful gases and the hydrochar particles are not prone to autoignition due to the high concentration of surface oxygen groups. In early investigations during the first decades of the twentieth century, hydrothermal carbonization was applied to different types of saccharides and biomass in order to try to understand the mechanism of coal formation [14,15]. In spite of the potential that hydrochar offers for sequestering atmospheric CO₂, no comprehensive study of this process or its products has yet been undertaken. Accordingly, the main aim of the present work is to investigate the chemical and structural properties of carbonaceous solids obtained through the hydrothermal

carbonization of biomass. Two representative biomass products were used for this purpose: a forest waste (eucalyptus sawdust) and an agricultural waste (barley straw).

2. Results and discussion

2.1. Structural characteristics of hydrochar samples

The hydrochar obtained has a brown colour consistent with a partially carbonized product. Inspection of this material by means of microscopy techniques revealed interesting changes in relation to the raw biomass. SEM images of the barley straw (Fig. 1a and b) and eucalyptus sawdust (Fig. 2a and b) show contrast SEM inspection of the materials resulting from hydrothermal carbonization (Fig. 1c-f and Fig. 2c-f for straw-based and for sawdust-based hydrochar products respectively) reveal substantial changes in the surface morphology of the particles. Numerous sphere-like microparticles can be seen on the surface of the larger particles. These microspheres probably have their origin to the decomposition of cellulose during hydrothermal carbonization, as we recently reported [11]. However, in the case of lignin, due to its greater chemical stability, only partial degradation occurs and the original skeleton of the particles is mainly preserved.

The texture of the hydrochar samples was analyzed by means of nitrogen physisorption. These materials were found to have a poor porosity, the BET surface area values being 4.4 and 8.3 m² g⁻¹ for the eucalyptus sawdust and barley straw-derived hydrochar respectively. In Fig. 3a the N₂ sorption isotherms of the hydrochar and the biochar sample, both obtained from barley straw, are compared. It can be seen that, whereas the biochar sample exhibits an isotherm typical of microporous materials and a relatively large BET surface area (153 m² g⁻¹), the hydrochar has a small BET surface area (8.3 m² g⁻¹) and a large nitrogen adsorption uptake for $p/p_0 > 0.9$ which suggests

that the surface area measured matches the external surface area (i.e. there are no framework-confined pores). In order to assess the hydrophilic character of the hydrochar and biochar materials, we carried out water vapor adsorption experiments (Fig. 3b). The amount of water adsorbed was normalized on the basis of the surface area. It was found that the H-B hydrochar sample adsorbed a substantially larger amount of water than the biochar, thereby revealing a greater water affinity (hydrophilic).

2.2. Chemical properties of hydrochar products

Table 1 shows the elemental chemical composition of the raw materials (eucalyptus sawdust and barley straw) and carbonized products. As was previously mentioned in relation to the hydrochar materials obtained through the hydrothermal carbonization of pure saccharides (glucose, sucrose, starch and cellulose) [10,11], we observed an increase in carbon content, together with a reduction in the amount of oxygen and hydrogen, in the conversion of the raw material to hydrochar. More specifically, the carbon content varied from $\sim 470 \text{ g}\cdot\text{kg}^{-1}$ for the raw biomass to $\sim 700 \text{ g}\cdot\text{kg}^{-1}$ for the hydrochar products. The changes in elemental composition from the raw materials (sawdust and straw) to the hydrochar products are consistent with a carbonization process and they were analyzed with the aid of the Van Krevelen diagram (see Fig. 4) [16]. It can be seen that the evolution of the H/CeO/C atomic ratios from the raw material to the hydrochar basically follows the trend corresponding to a dehydration process, similar to that previously observed in the hydrothermal transformation of simple saccharides such as glucose, sucrose or starch [10]. However, there is a slight deviation from the diagonal line, which suggests that decarboxylation is also taking place. The results obtained for the biochar sample prepared from barley straw are presented in Table 1 and Fig. 4. A discussion of these results is presented in the Supplementary Information (Section 2).

The hydrochar yield was found to be around $400 \text{ g}\cdot\text{kg}^{-1}$ for eucalyptus sawdust, which is slightly higher than that obtained for the barley straw ($\sim 370 \text{ g}\cdot\text{kg}^{-1}$). On the other hand, the percentage of carbon originally present in the raw material that is retained in the final solid product is very similar for both materials, around 56%. The fact that around 56% of the carbon in the original raw materials is retained in the hydrochar products suggests that a large fraction of the carbon contained in the biomass could be stored in this way. The rest of the carbon ($\sim 44\%$) is mainly contained in the organic compounds (i. e. furfural, hydroxymethylfurfural, organic acids, aldehydes, etc) that are dispersed in the aqueous phase [17-20]. These chemical substances are very valuable and their recovery would be the next logical step were hydrothermal carbonization to be introduced on a large scale. Furthermore, it is worth mentioning that at the end of hydrothermal process, once the reactor has cooled down, there is only a slight overpressure inside the vessel, which suggests that only a small amount of gaseous products are generated during hydrothermal carbonization.

The chemical transformations that took place during hydrothermal carbonization were examined with the aid of spectroscopic techniques (i.e. IR, Raman and XPS). The FTIR spectra obtained for the raw materials and their corresponding hydrochar samples are presented in Fig. 5. A detailed analysis of the FTIR spectra of eucalyptus sawdust and barley straw can be found in the literature [21,22]. The bands identified in the FTIR spectrum of eucalyptus sawdust for wavenumbers $< 2000 \text{ cm}^{-1}$ were assigned as follows: (i) 1730 and 1660 cm^{-1} to C=O stretching vibrations (conjugated and non-conjugated keto-carbonyl groups, respectively); (ii) 1600 and 1510 cm^{-1} to aromatic ring vibrations of the lignin (the latter mainly in guaiacyl units); (iii) 1465 and 1427 cm^{-1} to C-H deformation in the lignin and carbohydrates; (iv) 1378 cm^{-1} to C-H deformation in the cellulose and hemicellulose; (v) 1330 cm^{-1} to the ring breathing

vibrations characteristic of syringyl units in lignin; (vi) 1240 and 1270 cm^{-1} to the ring breathing vibrations characteristic of guaiacyl units (the latter appearing as a shoulder in the 1240 cm^{-1} band); (vii) 1163 cm^{-1} to C-O-C vibrations in the cellulose and hemicellulose; (viii) 1131 cm^{-1} to aromatic skeletal and C-O stretching vibrations and (ix) 900 cm^{-1} to C-H deformation in the cellulose [21]. The FTIR spectrum of the barley straw is similar to that of the eucalyptus sawdust and it differs only in the intensity of some peaks due to the different lignin/holocellulose (cellulose+hemicellulose content) contents of the raw materials. Thus, in the case of barley straw, the C=O stretching band (1720 cm^{-1}) is less intense than the C=C stretching band (1610 cm^{-1}), whereas in the eucalyptus sawdust both bands are equally intense. The bands in the $1000\text{-}1500\text{ cm}^{-1}$ region, which are associated to lignin, also differ in intensity between the two raw materials. The FTIR spectra of the hydrochar samples, are noteworthy for the absence of bands characteristic of cellulose such as the bands at 900 cm^{-1} (C-H deformation) and 1163 cm^{-1} (C-O-C vibration). In contrast, the bands characteristic of lignin (aromatic structure) are preserved, although they have shifted to lower or higher wavenumbers. Thus, the bands associated to aromatic ring vibrations have shifted to higher wavenumbers, 1515 and 1620 cm^{-1} , while the band attributed to C=O vibrations (carbonyl, quinone, ester or carboxyl) has shifted to a lower wavenumber, i.e. 1710 cm^{-1} , the band at 1660 cm^{-1} attributed to non-conjugated ketocarbonyl groups having completely disappeared. The wide band at $3000\text{-}3700\text{ cm}^{-1}$, attributed to O-H stretching vibrations in the hydroxyl or carboxyl groups, is present both in the raw materials and their hydrochar products. Also preserved in the hydrochar samples is the band at $3000\text{-}2830\text{ cm}^{-1}$, which corresponds to stretching vibrations of aliphatic C-H, suggesting the presence of aliphatic and hydroaromatic structures. On the other hand, new bands appear in the $875\text{-}750\text{ cm}^{-1}$ region, which are assigned to

aromatic CeH out-of-plane bending vibrations. Finally, the bands at 1320, 1215, 1114 and 1030 cm^{-1} , attributed to CeO stretching vibrations in hydroxyl, ester or ether, and the band at 914 cm^{-1} , attributed to O-H bending vibrations, suggest an abundance of oxygenated groups in the hydrochar samples. The FTIR spectra of barley H-B differ from those of H-E in the intensity of the bands at 1215 and 1114 cm^{-1} (C-O stretching vibrations), which are more intense in H-E than in H-B.

The presence of aromatic carbon structures in the hydrochar samples was also been confirmed by Raman spectroscopy. These samples exhibit spectra typical of carbonized materials [23], as shown in Fig. 6a. Thus, the Raman spectra contain two broad overlapping bands at around 1360 (D-mode) and 1587 (G-mode) cm^{-1} , which evidence the presence of C sp^2 atoms in benzene or condensed benzene rings in amorphous (partially hydrogenated) carbon [24]. This indicates that the hydrochar samples contain small aromatic clusters.

The oxygen functionalities present on the outer surface of the hydrochar particles were analyzed by X-ray photoelectron spectroscopy (XPS). The C 1s core level spectra obtained for the hydrochar samples, together with the peak-fitting of its envelope, are shown in Fig. 6b. For both materials the C 1s envelope contains three signals attributed, respectively, to the aliphatic/aromatic carbon group (CH_x , C-C/C=C) (284.6 eV), the hydroxyl groups (-C-OR) (286.1-286.2 eV), the carbonyl groups ($>\text{C}=\text{O}$) (287.7 eV) (only detected in the eucalyptus sawdust-derived hydrochar) and the carboxylic groups, esters or lactones (-COOR) (288.5 eV) (only detected in the barley straw-derived hydrochar) [25,26]. It is interesting that the surface of the eucalyptus sawdust-derived hydrochar products contain mainly hydroxyl groups, the proportion of these groups being considerably larger than in the barley straw-derived hydrochar. The XPS results point to a high concentration of oxygenated groups on the surface of the microparticles

of both hydrochar products, although the nature of these groups is different in each case. A comparison of the (O/C) atomic ratios determined by elemental analysis (0.269 and 0.200 for H-E and H-B respectively) with those calculated by XPS (0.318 and 0.298 for H-E and H-B, respectively) reveals that the outer layer of the hydrochar particles has a higher oxygen content than the inner part. This suggests that oxygen has accumulated at the periphery of particles, probably due to the transformation of cellulose that occurs during hydrothermal carbonization, as we previously reported [11]. In fact, in our opinion, this process causes the extraction of the cellulose from the lignocellulosic matrix and its subsequent conversion to carbonaceous microspheres which are then deposited on the outer surface of hydrochar particles, as evidenced by the SEM images (Figs. 1 and 2). In contrast, presumably due to the hydrothermal conditions, the lignin undergoes only minor changes and occupies the core of the hydrochar particles. Clearly, the high oxygen content of the outer layer of the hydrochar particles is associated to the cellulose-derived carbonaceous microspheres. This is supported by the fact that the values for the O/C atomic ratio deduced from the XPS spectra are close to those obtained for the hydrochar microspheres from the pure cellulose [11].

Since the biochar and hydrochar processes may be of considerable importance for CO₂ biosequestration, we were particularly interested in comparing the structural and chemical properties of these two materials. To this end, we prepared a biochar sample from the pyrolysis of barley straw, as described in the experimental section. In Section 2 of the Supplementary Information, we provide a comparative analysis of the characteristics of the hydrochar and biochar products.

3. Conclusions

In summary, we have demonstrated that hydrothermal carbonization is a straightforward low-tech process by means of which biomass can be converted into a carbonaceous

solid (hydrochar) containing around 50-60% of the carbon originally present in the raw material. This process was applied to two characteristic biomass materials (eucalyptus sawdust and barley straw). The chemical characteristics of the hydrochar products were found to be similar in both cases. We observed that the hydrochar particles are covered by microspheres (1-10 μm) which were probably caused by the severe chemical transformations that affect the cellulose fraction of the biomass during hydrothermal carbonization. From a chemical point of view, the hydrochar products exhibit a high degree of aromatization and they contain around 70 wt % of carbon and 21-25 wt % (daf) of oxygen. Oxygen is more abundant in the cellulose-derived microspheres and is associated with several types of functional groups (i.e. carbonyl, carboxylic, hydroxyl, quinone, ester, etc) as was deduced by IR and XPS spectroscopic techniques. The presence of these oxygen-containing groups

4. Experimental

4.1 Raw materials

The biomass samples used in this study were eucalyptus sawdust and barley straw. The sawdust was collected from a local sawmill (Avilés, Spain) and it constitutes a residual product generated from the treatment of eucalyptus wood (*Eucalyptus globulus*) of around 15 years old (harvested in 2008), which grown in Asturias (43°33' N 5°54' W, Spain). For these experiments, a sawdust fraction of <0.5 mm was separated (by sieving) from the as received material and stored in air at room temperature. The barley (*Hordeum vulgare* L.) straw was supplied by Antonio Fuertes (the father of A. B. Fuertes) who cultivated and harvested this plant in San Román de los Caballeros (42°38' N 5°50' W, Spain). This material was used as received.

4.2. Preparation of the hydrochar samples

The hydrothermal carbonization of the biomass samples was carried out according to the following procedure. Around 8 g of previously dried sawdust or straw was dispersed in 50 mL of distilled water. The mixture was kept under stirring for around 5 h at room temperature in air and, then, it was transferred to a stainless steel autoclave, which was heated up to 250°C at a heating rate of around 4 °C min⁻¹ (pressure at 250 °C of around 4 MPa). It was maintained at this temperature for 2 h. The solid product (hydrochar) was recovered by filtration, washed with distilled water and dried in air at 120 °C for 3 h. The hydrochar samples obtained from the eucalyptus sawdust and barley straw were denoted as H-E and H-B respectively.

For comparison purposes, a biochar sample was prepared from barley straw. To obtain this product, a certain amount of straw was treated under nitrogen flow (at atmospheric pressure) up to 400°C (3 °C min⁻¹) and maintained at this temperature for 2 h. This sample was denoted as B-B.

Characterization

Scanning electron microscopy (SEM) microphotographs were obtained with a Zeiss DSM 942 microscope. Diffuse reflectance Fourier-Transform Infrared (FTIR) spectra of the powders of the materials were recorded on a Nicolet Magna-IR 560 spectrometer fitted with a diffuse reflection attachment. The Raman spectra were recorded with a Horiba (LabRam HR-800) spectrometer. The source of radiation was a laser operating at a wavelength of 514 nm and a power of 25 mW. X-ray photoelectron spectroscopy (XPS) was carried out by means of a Specs spectrometer, using MgK α (1253.6 eV) radiation from a double anode at 150 w. Binding energies for the high-resolution spectra were calibrated by setting C 1s at 284.6 eV. Nitrogen adsorption measurements were performed at 77 K using a ASAP 2020 (Micromeritics) volumetric adsorption system. Water adsorption measurements were carried out at 25°C using a Hydrosorb

(Quantachrome) equipment. The elemental analysis (C, H and N) of the samples was carried out in a LECO CHN-932 microanalyzer.

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Table 1. Chemical characteristics and product yields for the raw materials and the hydrochar materials resulting from the hydrothermal treatment of eucalyptus sawdust and barley straw, and pyrolysis (Biochar) of barley straw.

Sample	Chemical composition (g·kg ⁻¹)					Atomic ratio (d.a.f.) ^b		Yield (g·kg ⁻¹) ^c	Carbon fixed (%) ^d
	C	H	O ^a	N	Ash	(O/C)	(H/C)		
Eucalyptus sawdust	480	58.7	454	1.5	6.2	0.710	1.47	-	-
H-E (Hydrochar)	697	47.1	250	1.0	5.4	0.269	0.811	400	57
Barley straw	468	56.5	414	18.5	43	0.664	1.45	-	-
H-B (Hydrochar)	699	50.3	200	7.5	43	0.200	0.803	370	56
B-B (Biochar)	725	24.2	111	6.3	134	0.115	0.400	310	48

^a Estimated by difference [O=1000-(C+H+N+Ash)]; ^b d.a.f. = dry ash free basis; ^c The yield is expressed as: (g product kg⁻¹ raw material); ^d Percentage of carbon contained in the raw material that is retained in the carbonized sample.

Figure 1. SEM images of the barley straw (a, b) and the barley straw hydrochar samples (c, d, e, f).

Figure 2. SEM images of the eucalyptus sawdust (a, b) and the eucalyptus sawdust hydrochar samples (c, d, e, f).

Figure 3. Nitrogen (a) and Water (b) sorption isotherms for the hydrochar (H-B) and biochar (B-B) samples obtained from barley straw.

Figure 4. Van Krevelen diagram of eucalyptus sawdust, barley straw and the carbonized samples resulting from hydrothermal treatment (hydrochar) and pyrolysis (Biochar).

Figure 5. FTIR spectra of: (a) pristine and hydrothermally carbonized eucalyptus sawdust (H-E) and (b) pristine (data extracted from ref. [22]) and hydrothermally carbonized barley straw (H-B).

Figure 6. Raman spectra (a) and C 1s core level spectra (b) of hydrothermally carbonized eucalyptus sawdust (H-E) and barley straw (H-B). Insets of Figure (b): general XPS spectra.