



# Parametric study of the hydrothermal carbonization of cellulose and effect of acidic conditions



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## ABSTRACT

Microcrystalline cellulose has been used to develop carbonaceous materials by hydrothermal synthesis. The use of HCl in different concentrations modifies the nature of the obtained materials. Surface area, determined by CO<sub>2</sub> adsorption, can be used to define a new empirical parameter, the “hydrothermal index” (H.I.), which allows a simple comparison of the different hydrothermal conditions. Higher temperature, longer time and higher HCl concentration produce, at the beginning, an increase in surface area up to a maximum of 386 m<sup>2</sup>/g, whereas harsher conditions beyond this limit decrease the surface area up to values around 100 m<sup>2</sup>/g. Carbon and oxygen content of the hydrothermal carbons nicely correlate with this hydrothermal index. However, the HCl concentration affects more directly to other properties, such as the particle size and morphology, the carbon yield, or the distribution of functional groups. This is due to the co-existence of at least two hydrothermal pathways, one in solution after cellulose hydrolysis and another one in solid phase. The prevalence of one mechanism or another depends on the variations in the individual rates of the reactions involved in the hydrothermal process.

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## 1. Introduction

Lignocellulosic biomass is a renewable and accessible feedstock for the production of commodity chemicals and fuels [1]. The main component of raw biomass is cellulose, which is a biopolymer made from glucose monomers. The hydrothermal treatment of cellulose was first developed to hydrolyse cellulose into liquid fuels or platform chemical molecules such as furfurals [2–5]. The treatment of cellulose in water under pressure, at temperatures in the 150–400 °C range, gives rise to a mixture of soluble organic substances and a carbon-rich solid product, the relative amount of each one depending on the treatment conditions. At very high temperatures (>300 °C) and pressures (25 MPa, supercritical water) the hydrolysis of cellulose gives rise mainly to soluble organic substances [6–8]. When a dissolved organic molecule is searched for, the solid product termed sometimes as humins or hydrochar is considered an undesired by-product [9]. Only recently, attention has been paid to the solid resulting from hydrothermal treatment

[10–12]. It is widely reported that the hydrothermal treatment of monosaccharides such as glucose produces carbon microspheres of uniform sizes under very mild process conditions [13–16]. Compared to glucose, cellulose is a more convenient feedstock because it is more abundant and inexpensive. Several authors have studied the hydrothermal carbonization of cellulose [17–20]. For the formation of hydrothermal carbon spheres, the hydrothermal carbonization of cellulose requires more severe conditions than that of glucose because first it has to be hydrolyzed to monomers. It is reported that the onset in the formation of the hydrothermal carbon spheres from cellulose occurs between 210 and 220 °C [19]. A mechanism of hydrothermal carbonization of cellulose was proposed consisting first in the hydrolysis of cellulose chains and fragmentation into soluble products (oligomers, glucose and isomerized products) followed by condensation, aromatization, nucleation and growth of the solid carbonaceous spheres. However, the chemical and spectroscopic characterization of carbonaceous materials prepared from cellulose at different temperatures and times of hydrothermal treatment revealed that this treatment leads to a material rich in aromatic groups, even at short times or low temperatures, in contrast to glucose that yields a polyfuran structure [18]. This result points to a major mechanism consisting into a modification of the cellulose by reactions such as intramolecular

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condensation, dehydration and decarboxylation. Since it is known that the hydrolysis of cellulose is promoted by acid catalyst [21], the mechanism through soluble intermediates should be promoted by strong acids, which also catalyze the subsequent condensation and dehydration reactions. Only the preparation of one hybrid hydrothermal carbonaceous material, from cellulose and ovalbumin, has been described in acidic medium [17], but as far as we know, there is no systematic study of hydrothermal carbonization of cellulose to produce solid carbon in the presence of acids. Here we describe the hydrothermal carbonization of cellulose adding low-concentrated solutions of HCl. Herein, the effect of the temperature, treatment time and HCl concentration have been studied and compared with the hydrothermal carbonization without acid addition. The temperature range has been selected as low as possible and around that in which the onset of hydrothermal carbon spheres formation occurs (195–215 °C).

## 2. Experimental

For the preparation of hydrothermal carbon, 2 g of microcrystalline cellulose (Merck) were introduced in a Teflon-lined autoclave. Subsequently, 10 ml of either pure distilled water, or 2 M HCl solution, or 5 M HCl solution were added to the autoclave. The autoclave was closed and introduced in an oven at the desired temperature (195 °C or 215 °C) and it was maintained inside the oven during the desired time (20 or 40 h).

The yields of the final solid residues obtained upon hydrothermal carbonization were determined using the following formula:

$$\text{HTC yield \%} = \frac{\text{amount of recovered solid after HTC (g)}}{\text{initial amount of cellulose (g)}} \times 100$$

The elemental analysis (C,H,N,S) was carried out in a Thermo-fisher Flash 1112 elemental analyzer. The elemental analysis technique is based in the instant and complete oxidation of the sample using the combustion with pure oxygen at a temperature of around 900 °C. The sample is ground to a particle size smaller than 80 µm and combusted in tin capsules after mixing with an oxidant (V<sub>2</sub>O<sub>5</sub>) with an oxygen amount adjusted to each sample while flowing He. The different combustion products are transported using a carrier gas (He) through an oxidant bed of CuO at 900 °C to oxidise them to SO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>O and CO<sub>2</sub>. Subsequently, they flow through a reduction bed of metallic Cu at 550 °C that only reduces NO<sub>x</sub> to N<sub>2</sub>. Subsequently, the resulting gases are selectively separated in specific chromatographic columns, selectively desorbed by heating and analysed in a thermal conductivity detector (TCD) where the signal is proportional to the concentration of each gas. The TCD detector was calibrated with sulfanilamide. Since the raw material (cellulose) does not contains other elements than C,H and O, the oxygen content was determined by difference.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash of Si(Li). The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal. The mean particle size was determined by measuring 100 particles from images at different locations of the sample.

CO<sub>2</sub> adsorption (Dubinin-Radushkevich) was determined at 273 K using a Micromeritics ASAP 2020 apparatus after outgassing for 4 h at 423 K. For the estimation of the surface area, the Dubinin–Astakhov equation [22] has been used, which represents a refinement of the Dubinin–Radushkevich equation for carbons with non-uniform pores [23–25].

The total amount of acid sites on each catalyst was determined by back titration. The solid (≈ 30 mg) was added to 25 ml of 0.01 M

NaOH solution and allowed to equilibrate under stirring for 1 h. Thereafter, it was titrated with 0.05 M potassium hydrogen phthalate solution using a Crison pH Burette 24.

NMR spectra were recorded in a Bruker Avance III WB400 spectrometer with 4 mm zirconia rotors spun at magic angle in N<sub>2</sub> at 10 kHz. <sup>1</sup>H–<sup>13</sup>C CP (cross-polarization) spectra (up to 10000 scans) were measured using a <sup>1</sup>H π/2 pulse length of 2.45 µs, with a contact time of 2 ms, and spinal64 proton decoupling sequence of 4.6 µs pulse length.

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer in configuration theta-theta using nickel-filtered CuK α radiation (wave length = 1.54 Å), a graphite monochromatic source and scintillation detector. 2θ angles from 3 to 80° were scanned with a length step of 0.05 and an accumulation time of 3 s.

## 3. Results

The hydrothermal carbonization starting from microcrystalline cellulose aqueous solution was carried out varying two experimental conditions, namely the temperature (195–215 °C) and the time (20–40 h). The XRD patterns (Fig. S1, Supplementary material) demonstrated that the carbons are amorphous in nature with no detectable crystalline phases.

Yields of solid residue after the different hydrothermal treatments and elemental analyses are gathered in Table 1. In the absence of HCl, yield of carbonaceous materials in the range of 30–42% are obtained, with 50–69% recovery of the carbon content of the starting cellulose, values comparable to those described in previous papers under similar conditions [18,19], with a significant increase as a function of the treatment time. These values are slightly higher than the yields obtained from glucose under the same conditions. The use of HCl produces a significant decrease in the yield of solid material, from 14 to 21% with 2 M HCl, and values around 25% with 5 M HCl. In both cases, the temperature and the time under hydrothermal conditions have a less pronounced effect on the final yield.

Compared to the starting cellulose, the solid residue is enriched in carbon because the oxygen content decreases to the half, from 50.7% for pristine microcrystalline cellulose to 27.1% and 25.3% after 20 h treatment in the absence of HCl at 195 °C and 215 °C, respectively. The temperature increase from 195 to 215 °C entails only a slight reduction of oxygen content. For longer treatment durations (40 h) the oxygen content not only does not decrease further but also slightly increases, suggesting that the increased carbon yield with time of treatment is mainly due to the condensation of soluble products without further dehydration. On the contrary, when HCl is present the oxygen content decays as the treatment time, the HCl concentration and the temperature increase. This suggest that the HCl acid catalyses the dehydration/deoxygenation. Likewise, the lowest O content of 12.8% is attained using the highest HCl concentration (5 M), highest temperature (215 °C) and time (40 h).

The total acidity has been determined by titration with NaOH. The results (Table 1) show a wide variability, from 0.85 to 2.31 mmol/g but, in any case, they are values far below the acidity of the hydrothermal carbon prepared from glucose (Glu-195-20h).

The SEM images of pristine cellulose show a fibrous structure with some microstructural features (Fig. 1a and b). This morphology changes after hydrothermal treatment to different extents depending on the treatment conditions. SEM images of the solid residue after 20 h of treatment at 195 °C in absence of HCl reveal the presence of smaller fibres stemming from cellulose fragmentation which are coated by microspheres (Fig. 1c and d). After 40 h of treatment at 195 °C (Fig. 1e and f), the structure of the

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