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 CO₂ 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 m²/g, whereas harsher conditions beyond this limit decrease the surface area up to values around 100 m²/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 a 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 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 2M 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:

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

The elemental analysis (C,H,N,S) was carried out in a Thermofisher 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 (V₂O₅) 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 SO₂, NO_x, H₂O and CO₂. Subsequently, they flow through a reduction bed of metallic Cu at 550 °C that only reduces NO_x to N₂. 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

CO₂ 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 ($\approx$ 30 mg) was added to 25 mL of 0.01M 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 N₂ at 10 kHz. ¹H–¹³C CP (cross-polarization) spectra (up to 10000 scans) were measured using a ¹H $\pi/2$ pulse length of 2.45 μ s, with a contact time of 2 ms, and spinal64 proton decoupling sequence of 4.6 μ s 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. 2 θ 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). This XRD pattern (Figure S1 supplementary material) demonstrated that the carbons are amorphous in nature with no detectable crystalline phase.

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 2M HCl, and values around 25% with 5M 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 (5M), highest temperature (215 °C) and time (40 h).

Table 1. Yields and elemental analysis of hydrothermal carbons prepared from microcrystalline cellulose.

	Yield (%) ^a	C (wt%)	H (wt%)	O (wt%)	C yield (%) ^b	Acidity (mmol/g) ^c
Glu-195-20h	28.4	66.3	4.4	29.9	47.1	3.42
Cel	-	42.9	6.2	50.7	-	-
Cel-195-20h	32.3	68.3	4.5	27.1	51.4	2.31
Cel-195-40h	41.0	67.8	4.3	27.6	64.8	n.d.
Cel-215-20h	30.5	70.0	4.5	25.3	49.7	2.09
Cel-215-40h	42.2	69.7	4.5	25.6	68.6	n.d.
Cel-195-2M-20h	14.3	67.6	4.4	27.9	22.5	1.94
Cel-195-2M-40h	19.0	69.6	4.7	25.7	30.8	n.d.
Cel-215-2M-20h	18.6	74.5	5.1	20.4	32.3	n.d.
Cel-215-2M-40h	21.0	77.2	5.7	17.1	37.8	1.37
Cel-195-5M-20h	24.7	73.5	5.1	21.4	42.4	0.85
Cel-195-5M-40h	26.4	75.3	5.6	19.0	46.3	1.28
Cel-215-5M-20h	25.9	77.1	5.5	17.3	46.5	n.d.
Cel-215-5M-40h	26.6	81.1	6.0	12.8	50.3	n.d.

^a Mass of final solid per mass of starting cellulose. ^b Percentage of carbon retained from the C content in the starting cellulose. ^c Determined by titration.

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).

Figure 1. Representative SEM images of pristine cellulose microfibers (a,b) and solid product after hydrothermal carbonisation of 0.2 mg ml^{-1} aqueous microcrystalline cellulose dispersion at 195°C for two different durations: (c,d) hydrothermal treatment for 20 h, (e,f) hydrothermal treatment for 40 h

The SEM images of pristine cellulose show a fibrous structure with some microstructural features (Figure 1a,b). This morphology changes after hydrothermal treatment to different extents depending on the treatment conditions. The mean size of the spheres (Table 2) also changes with the hydrothermal conditions. In general, the size of microspheres is larger in the presence of HCl and it decreases with time in absence of HCl but remains quite similar or increases in the presence of HCl. 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 (Figure 1c,d). After 40 h of treatment at 195°C (Figure 1e,f), the structure of the pristine microfibrils has almost vanished and only aggregates of nanospheres are observed. The increase of temperature to 215 °C apparently accelerates the process of microfiber fragmentation and formation of nanospheres since the microstructure of the original microfibrils is not already observed after 20 h (Figure 2a,b) in contrast to the observation at 195°C (Figure 1c,d) for the same time. It is also apparent that the carbon spheres are smaller after 40 h than after 20 h, both at 195 °C and 215 °C.

Figure 2. Representative SEM images of hydrothermal carbonisation of 0.2 mg ml⁻¹ aqueous microcrystalline cellulose dispersion at 215°C for two different durations: (a,b) hydrothermal treatment for 20 h, (c,d) hydrothermal treatment for 40 h.

The reduction in the size of the spheres as the time increases could be attributed either to the shrinking of initial solid spheres due to further internal condensation or to the precipitation of smaller solid spheres produced by condensation of highly diluted soluble oligomers. The later explanation seems more plausible since there is an increase of solid yield with the time.

Figure 3. Representative SEM images of hydrothermal carbonisation of 0.2 mg ml⁻¹ aqueous microcrystalline cellulose dispersion and 2 M HCl at 195°C for two different durations: (a,b) hydrothermal treatment for 20 h, (c,d) hydrothermal treatment for 40 h

Comparison of Figure 3 with Figure 1 clearly reveals that the presence of 2M HCl enhances the fragmentation of cellulose microfibrils and the formation of carbon spheres. There is no trace of the fibrous structure of the pristine cellulose after 20 h of treatment

at 195 °C in 2M HCl (Figure 3a,b) while, in the absence of HCl, cellulose microfibril fragments were still visible (Figure 1c,d). This pinpoints that acidic medium catalyses hydrolysis and dissolution reactions, having an effect similar to increasing temperature in the absence of HCl. At the highest temperature of 215°C in the presence of 2M HCl (Figure 4), some larger globular particles that are not found in the other solids are observed. They can be produced by the growth of some smaller nanospheres as the time of treatment increases.

Figure 4. Representative SEM images of hydrothermal carbonisation of 0.2 mg ml⁻¹ aqueous microcrystalline cellulose dispersion and 2 M HCl at 215°C for two different durations: (a,b) hydrothermal treatment for 20 h, (c,d) hydrothermal treatment for 40 h

The different concentration of HCl also affects the structure of the produced solid. Surprisingly, the solid attained after treatment using 5 M HCl at 195°C (Figure 5) resembles the fibrous structure of the pristine cellulose microfibrils but with a surface covered with condensed nanospheres, while only the nanosphere were observed for the solid obtained using 2M HCl (Figure 3). At higher temperature (215°C) the hydrolysis

and fragmentation must be enhanced because the structure of the pristine microfibers is barely observed (Figure 6) and the formation of nanosphere aggregates by condensation reactions is favored leading to the maximum carbon yield in the presence of HCl and minimum oxygen content of the solid.

Figure 5. Representative SEM images of hydrothermal carbonisation of 0.2 mg ml^{-1} aqueous microcrystalline cellulose dispersion and 5 M HCl at 195°C for two different durations: (a,b) hydrothermal treatment for 20 h, (c,d) hydrothermal treatment for 40 h

Figure 6. Representative SEM images of hydrothermal carbonisation of 0.2 mg ml^{-1} aqueous microcrystalline cellulose dispersion and 5M HCl at 215°C for two different durations: (a,b) hydrothermal treatment for 20 h, (c,d) hydrothermal treatment for 40 h

The textural properties of the hydrothermal carbons are important for different applications, such as their use of catalysts after sulfonation [26,27]. The micropore surface area and volume (Table 2) were measured by CO_2 adsorption at 273 K because the accessibility to this adsorbate to the narrow micropores of this type of materials is not restricted kinetically, in contrast with the measurements using N_2 at 77 K [28]. This method has been shown to be useful in the case of hydrothermal carbons [29]. As can be seen, the values of surface area and micropore volume show a great dispersion, from 104 to $386 \text{ m}^2/\text{g}$ and from 0.045 to $0.168 \text{ cm}^3/\text{g}$, with no clear trends at a glance.

Table 2. Textural parameters of hydrothermal carbons determined by CO₂ physisorption and mean particle size determined from SEM images

	Surface	Micropore pore	Pore volume micropores<1	Mean particle size
	Area m ² g ⁻¹	volume cm ³ g ⁻¹	μm cm ³ g ⁻¹	
Glu-195-20h	143	0.057	0.035	370
Cel-195-20h	201	0.083	0.039	120
Cel-195-40h	370	0.166	0.033	40
Cel-215-20h	220	0.092	0.041	180
Cel-215-40h	156	0.063	0.029	50
Cel-195-2M-20h	208	0.085	0.046	220
Cel-195-2M-40h	386	0.166	0.062	230
Cel-215-2M-20h	374	0.168	0.050	550
Cel-215-2M-40h	170	0.072	0.026	600
Cel-195-5M-20h	274	0.118	0.044	220
Cel-195-5M-40h	370	0.166	0.033	450
Cel-215-5M-20h	115	0.049	0.016	220
Cel-215-5M-40h	104	0.045	0.013	280

The ¹³C-CP-MAS-NMR spectra of the hydrothermal carbons prepared from cellulose (Figure 7) show three distinct zones. The most prominent one, at 100-160 ppm, corresponds to sp² carbons in aromatic rings. The zone corresponding to aliphatic sp³ carbons lays out between 10 and 60 ppm, whereas the carbonyl groups appear at 160-210 ppm. Compared with the hydrothermal carbon prepared from glucose, these materials show a lower contribution of the furanic carbons at 100-120 ppm (C_β) and 140-155 ppm (C_α), in comparison with the benzenic carbons around 120-130 ppm. The carbons from cellulose also show a slightly lower contribution of the aliphatic carbons, with a larger dispersion of signals, together with a lower amount of ketones at around 200 ppm and higher amount of carboxylic acids at 175 ppm. These are general trends, but the variation degrees depend on the hydrothermal conditions.

Figure 7. ^{13}C CP-MAS-NMR spectra of hydrothermal carbons: a) Glu-195-20h, b) Cel-215-20h, c) Cel-195-2M-40h, d) Cel-195-5M-40h, e) Cel-215-2M-40h.

4. Discussion

As pointed in the introduction, two types of hydrothermal mechanisms are proposed in the literature. One of them, called “soluble pathway” in Figure 8, is based in a first process of cellulose hydrolysis, favored at high temperature, to produce glucose and soluble oligomers, that evolve to furan derivatives by dehydration and then to carbon particles by condensation and polymerization processes [19]. In the “solid pathway”, the full cellulose molecule suffers processes of dehydration and condensation to give a modified polymer, called intermediate cellulose [30], that evolves to the final carbon material, incorporating soluble compounds by condensation reactions [18]. Thus, a change in the hydrothermal conditions may produce a shift in the major reaction pathway, with a subsequent modification of the final properties of the carbon material. Apparently, the critical

condition that determines the pathway is the concentration of HCl used in the hydrothermal process because acidity favours dissolution as deduced by the lower carbon yield in the presence of HCl and higher fragmentation observed by SEM.

From data of surface area (Table 2), it seems that softer hydrothermal conditions (lower temperature, short time, absence of HCl) leads to low surface values, whereas harder conditions increase those values up to a maximum, and beyond that point surface area decreases again.

Figure 8. Hydrothermal pathways from cellulose to carbon.

Thus, surface area was taken as an indication of the progress of the hydrothermal process. An empirical parameter “hydrothermal index” was calculated by taking the softest conditions with the lowest surface area (Glu-195-20h, 143 m²/g) and the maximum surface area (386 m²/g) as the limits of the rise range, and then the minimum surface area (104 m²/g) as the limit for the descent range, and considering both ranges as straight lines (Figure 9).

Figure 9. Evolution of the surface área (m²/g) (determined by CO₂ adsorption) of hydrothermal carbons as a method to calculate the empirical parameter “hydrothermal index”.

The values of the “hydrothermal index” (H.I.) were arbitrarily assigned as zero for the initial point (Glu-195-20h), 10 for the maximum area (Cel-195-2M-40h) and 20 for the minimum (Cel-215-5M-40h). The different hydrothermal conditions were placed either in the rise or in the descent range following the logical order for one of the conditions (H.I.: 40h > 20h, 5M > 2M > no HCl, 215 > 195), when the other two are kept constant

(see Supplementary Material). Only some single value (215-2M-20h, for example) cannot be unequivocally placed following this logic, but the result would not be too different (9.5 in the rise range, 10.4 in the descent range). In this way, two different hydrothermal conditions can be directly compared. For example, 195-40h are harder conditions (H.I. = 9.3) than 195-5M-20h (H.I. = 5.4) in spite of the use of HCl, showing that time is in this case more important. Thus, the other parameters of the hydrothermal carbons were correlated with H.I., trying to find any rationale in the results.

When the oxygen and carbon contents are represented against the H.I. (Figure 10 a and b) a clear trend is observed. Carbon content increases and oxygen content decreases with higher H.I. This fact is more evident for the solids prepared under harder conditions indicating a continuous dehydration process favoured by higher temperatures and acid concentrations.

a

b

Figure 10. Oxygen content (a) and carbon content (b) of the hydrothermal carbons vs the hydrothermal index. (■) carbons prepared at harder conditions (□) carbons prepared at lower temperatures and acid concentrations.

On the contrary, the yields, both mass and carbon yields, do not correlate with the H.I. A high dispersion of the results is obtained, and trends are only apparent when results are represented in three groups, corresponding to hydrothermal synthesis in the absence of HCl, with 2M HCl and with 5M HCl (Figure 11). In each group, straight lines are obtained in the graphs of yield vs H.I. The highest values are obtained without HCl, in agreement with the hypothesis of the “solid pathway” [18] and the lowest presence of soluble compounds. Harder conditions (higher H.I.) favor the condensation of the soluble materials with the intermediate cellulose, leading to higher yields. Surprisingly, Glu-195-20h nicely correlates in the same straight line, in spite of being a monomeric instead of a polymeric starting material, and this might indicate the existence of a pre-polymerization process from glucose under hydrothermal conditions. In fact, this possibility has been reported in the case of hydrothermal synthesis in the presence of HCl [31], and this would be also possible in the absence of acid.

Figure 11. Mass yields (filled symbols) and carbon yields (open symbols) of the hydrothermal synthesis under different conditions: without HCl (■), with 2M HCl (▲), and with 5M HCl (◆).

In the initial hypothesis, the use of HCl should promote the hydrolysis of cellulose, favoring the “soluble pathway”, and this seems to be confirmed by the low yields obtained at low H.I. with HCl. However, they are also lower than that obtained for Glu-195-20h (H.I. = 0), which seems to indicate that the presence of an acid in the medium significantly modifies the mechanism of the “soluble pathway”, in agreement with the results obtained in hydrothermal synthesis from glucose in acidic conditions [31]. Likely, the hydrolysis is quite fast in all cases, and yield is controlled by the condensation-polymerization processes, which seem to be more efficient with high concentration of HCl and high H.I. (harder conditions). The increase in the condensation degree accounts also for the decrease in surface area observed at higher values of H.I., whereas the hydrolysis and dehydration processes that predominate at low H.I. lead to increasing surface area.

These differences in yields, depending on the acidity of the hydrothermal medium, are also applicable to the morphology of the particles as seen by SEM. In the absence of HCl (Figures 1 and 2), the cellulose fibers are still visible in Cel-195-20h, indicating a low degree of hydrolysis and fragmentation of the starting material, in agreement with the “solid pathway”, with formation of nanospheres on microfiber surface. As conditions get harder (higher temperature and/or longer time), the fibrous structure disappears whereas yield increases with a reduction in the nanospheres size, indicating a transformation in solid state with condensation of soluble materials. The acidic conditions with 2M HCl favor the hydrolysis of cellulose, as also pointed by the lower yield of solid material, and the fibrous structure is not detectable at any stage of the hydrothermal process (Figures 3 and 4). However, although the hydrothermal process likely takes place through the “solution pathway”, the growing of the solid to increase the yields seems to proceed in the same way as in the absence of HCl, given that particles are also smaller at higher values of H.I. The solid prepared using 2M HCl at 195°C exhibits uniform particle size (Figure 3), whereas higher polydispersity is obtained at 215°C, which can be explained by a faster polymerization. Surprisingly, the use of 5M HCl preserves the fibrous structure of cellulose (Figures 5 and 6), probably due to a change in the relative reaction rates of all the processes involved in the hydrothermal synthesis. This result seems to indicate that the intramolecular dehydration and condensation reactions of cellulose (solid pathway)

prevail over the hydrolysis of the fibers and intermolecular condensation of the soluble materials. This is also in agreement with the higher yield obtained with 5M HCl in comparison with 2M HCl.

Although the use of CP in solid state NMR precludes the quantitative use of the signals, they can serve as a qualitative indication of the variations in the relative abundance of the different parts of the carbon materials. In Figure 12, the relative integrals of carbonyl (ketones), carboxylic (acids) and aliphatic carbons with respect to the total signal for aromatic carbons (taken as 100%) are represented vs the H.I. Each type of carbon shows a different evolution. Whereas carboxylic acids remain low (2-4%), independently from the hydrothermal conditions, both ketones and aliphatic carbons suffer a significant drop when changing from glucose (H.I. = 0) to cellulose, even under soft conditions. Then, aliphatic carbons remain constant (around 65%) at any H.I., whereas ketones decrease until values close to zero at high H.I.

Figure 12. Relative integrals of ketones (■), carboxylic acids (Δ) and aliphatic carbons (◇) in the ^{13}C -CP-MAS-NMR spectra with respect to aromatic carbons.

The deconvolution of the broad aromatic envelope (Figure 13) allows finding around 7-9 bands, that in the case of Glu-195-20h appear at 154, 149, 142, 134, 129, 123, 115, 109 and 103 ppm. The signals beyond 140 ppm have been assigned [32] to α carbon atoms in furan moieties, whereas those below 120 ppm should correspond to β carbon atoms. From

literature,^[33] the signals in these two zones can belong to different types of carbon atoms, as represented in figure 14, including furans and benzofurans, but also phenols, naphthols and the corresponding ethers. In general, quaternary carbons directly bound to oxygen appear in the range of 150-160 ppm, whereas tertiary ones do in the range of 140-150 ppm. In the case of carbons at low chemical shifts, it is more difficult to establish general rules and ranges. Given the difference in intensity of the signals for quaternary and tertiary carbon atoms and the uncertainty in the assignment of some of signals, it is very difficult to find an explanation for the evolution of the signals in the NMR spectra of hydrothermal carbons from cellulose. The only clear conclusion is the higher contribution of the aromatic carbons in non-oxygenated species (120-140 ppm range, Figure 13b,c), although there is no direct correlation with the H.I. or the oxygen content, as it can be present in different ways (ketone, carboxylic acid/lactone, phenol, furan).

Figure 13. Deconvolution (90-170 ppm region) of the ^{13}C CP-MAS-NMR spectra of hydrothermal carbons: a) Glu-195-20h, b) Cel-215-20h, c) Cel-195-5M-40h.

Figure 14. Oxygenated aromatic compounds and ^{13}C NMR chemical shifts in solution within the 140-160 ppm (bold) and 100-120 ppm (italic) ranges.

In the case of aliphatic carbons, the assignment is even less certain. Around seven peaks can be deconvoluted in the spectrum of Glu-195-20h (Figure 15a), with chemical shifts of 50, 44, 40, 35, 28, 22 and 13 ppm. The signal at 50 ppm has been assigned to methyne (CH) carbons, whereas mobile methyl (CH_3) groups appear at 13 ppm [32]. The rest of signals are difficult to assign, as they should belong to both mobile and rigid methylene groups (CH_2), as well as mobile methyl groups in different environments. Perhaps the most significant change in the aliphatic signals is the larger contribution of the signals at low chemical shift (≤ 20 ppm) at higher H.I., probably due to an increase in the number of terminal methyl groups.

Figure 15. Deconvolution (0-70 ppm region) of the ^{13}C CP-MAS-NMR spectra of hydrothermal carbons: a) Glu-195-20h, b) Cel-215-20h, c) Cel-195-5M-40h.

The variation in composition and contribution of the different functional groups has an effect on the acidity of the hydrothermal carbons. As can be seen in Figure 16, the acidity suffers a sharp decrease at low H.I. values, and it finally stabilizes at high H.I. This evolution does not correlate with that of the signal for carboxylic groups in NMR, but probably it reflects the decrease in aromatic C-O bonds, not only due to furanic groups but also to phenols, with respect to Glu-195-20h.

Figure 16. Evolution of acidity with hydrothermal index.

5. Conclusions

A series of carbonaceous materials have been prepared by hydrothermal synthesis using microcrystalline cellulose as starting material. Three parameters have been changed in the hydrothermal conditions, namely temperature, time and HCl concentration. The use of HCl significantly modifies the nature of the obtained materials, favoring hydrolysis and deoxygenation reactions. The surface area of the carbons, determined by CO₂ adsorption, increases with harder hydrothermal conditions (higher temperature, longer time, higher HCl concentration) up to a maximum of 386 m²/g at 195°C with 2M HCl for 40 h. From that point, the surface area decreases up to values around 100 m²/g. A new empirical parameter, the “hydrothermal index” (H.I.), has been defined taking the surface area results as an indication of the extent of the hydrothermal process. The carbon and oxygen contents of the hydrothermal carbons correlate with the H.I. On the contrary, other properties, such as the particle size and morphology, the yield, or the distribution of functional groups, do not directly correlate with the H.I., but they depend on a combination of conditions, mainly the HCl concentration. This has been explained by the existence of at least two hydrothermal pathways, one in solution after cellulose hydrolysis and condensation of the soluble species, and another one in solid phase, by modification of the cellulose itself. The concentration of HCl is the parameter that boost the occurrence of the soluble pathway while temperature favors condensation reactions. The change in

hydrothermal conditions modifies the prevalence of one or another mechanism, leading to solid materials with different morphological, textural and chemical properties.

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