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# Hydrocarbonization. Does It Worth to Be Called a Pretreatment?

*Silvia Román, Beatriz Ledesma, Andrés Álvarez-Murillo, Eduardo Sabio, J. F. González, Mara Olivares-Marín and Mouzaina Boutieb*

## Abstract

In this work, we aim to evaluate the potential of hydrothermal carbonization (also known as wet pyrolysis) as a pretreatment, by evaluating the changes induced in the raw material (cellulose) under varying experimental conditions. Hydrocarbonization processes were performed under different temperature, time and biomass/water ratios following a response surface methodology. The hydrochars obtained were characterized in terms of proximate analysis, behavior towards pyrolysis and combustion, heating value and surface textural and chemical features. The presence of typical hydrocarbonization reactions (dehydration, hydrolysis, decarboxylation, decarbonylation, recondensation, etc.) was only possible if a limit temperature (200°C) was used. Under these conditions, proximate analyses changed, the surface chemistry was modified, and the formation of a second lignite-type solid fraction was observed.

**Keywords:** hydrocarbonization, wet pyrolysis, cellulose, drying, energy efficiency, biomass

## 1. Introduction

As the consequences of the massive use of fossil fuels are more and more worrying, national and international strategies are pointing out the clear and immediate need of shifting the current energy supply infrastructures towards more environmental friendly and sustainable models. Geopolitical conflicts due to dependency relations between countries, next depletion and climate change issues involve a severe reality that is at the moment causing wars, increasing human inequality, jeopardizing food security and triggering human relocation processes, which cause more and more international conflicts [1].

One purposeful renewable energy source with proven potential to provide heat or biofuels is biomass. Estimates conclude that a shift to biological raw materials could save up to 2.5 billion tons of CO<sub>2</sub> equivalent per year by 2030, increasing markets for bio-based raw materials and new consumer products several-fold [2].

Regarding biomass sources, their abundance and availability, decentralization, ease to extract and handle and heating value are very precious features. There are, however, some issues that limit the use of some biomass resources, as for

example, their high moisture content, which involves the implementation of cost-intensive drying pretreatments before classical thermochemical processes such as pyrolysis, combustion or gasification.

One pretreatment that has recently gained prominence is hydrocarbonization (HTC) or wet pyrolysis, that is, the thermochemical conversion of biomass in hot compressed water under relatively low temperature and self-generated pressure. In this way, biomass moisture is not a downside, but takes a role in the reaction both as solvent and as catalyst, triggering the reaction. Because of this important advantage as well as other additional features related to the final product quality, ease, low cost or process energy efficiency, this technique has gained relevance during last years. Because of the abovementioned advantages, HTC processes have been more and more used during last years and researchers have mainly focused their attention on (a) studying it as a previous reactions step for other processes, or (b) investigating HTC as a process to yield a material suitable for specific applications such as biofuel, adsorbent, soil amendment or catalyst [3].

In previous works, we studied the potential of HTC processes to upgrade tomato peel, olive pomace and orange peel [4–6]. Other authors have addressed the HTC of other humid materials such as waste streams [7], grape pomace [8] or potato peel [9]. In this work, we aim to evaluate the changes induced by HTC on pure cellulose that can affect to their further use in other thermochemical processes. Based on the experimental results obtained by HTC under varying experimental conditions, as well as the results found in the bibliography, we aim to offer insight about the chemical and structural changes induced as a result of the process, and their potential influence in further processing of the raw material.

## **2. Experimental**

### **2.1 Hydrocarbonization experiments**

Microcrystalline cellulose (Sigma-Aldrich) was dried at 105°C until constant weight and then stored in closed flasks placed in desiccators for further analysis.

The HTC processes were performed in a stainless steel autoclave (Berghof, Germany). In a 0.2 L Teflon vessel (unstirred), an appropriate amount of sample (5–18.4 g) and 150 mL of deionized water at room temperature were added, in order to obtain the targeted biomass/water ratio, R (1.1–12.3%). Then, the Teflon vessel was sealed and placed into the autoclave and the system remained overnight at room temperature. Thereafter, the system was heated up in an electric furnace at selected temperatures (150–250°C), during a chosen processing time (3.2–36.8 h). The experimental conditions were designed according to the response surface methodology, as described elsewhere [5]. Following this procedure, 18 runs were performed (15 under different conditions, and 3 additional runs at one particular condition to test experimental variability, as stated by the method).

The reactor pressure was always at or slightly above the water vapor pressure. After the reaction, the system was cooled down using an ice bath and then the autoclave was opened and the solid product (Hydrochar, HC) was obtained by vacuum filtration (Whatman filter paper number 3). Then, the HCs were dried for 24 h and stored in a desiccator for further analysis.

### **2.2 Characterization of hydrochars**

Both pure cellulose and derived HCs were characterized in terms of their proximate analysis (% wt./wt.) following the technical specifications CEN/TS 1474–2,

CEN/TS 15148 and CEN/TS 14775 for moisture (M), volatile matter (VM) and ash (A), respectively. Fixed carbon was determined by difference (100-M-VM-A).

The thermogravimetric behavior of the raw material and the derived HCs was studied under both air and nitrogen atmospheres, using a thermobalance (TA Instruments) using a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a gas flow of  $100\text{ mL min}^{-1}$  in both cases, as described elsewhere [10]. In order to get further knowledge on the thermal degradation profiles, selected samples were analyzed by coupled thermogravimetric and mass spectrometry analysis (TG/MS, thermogravimetric system, TA Instruments; Mass Spectrometer, Pfeiffer Tecnovac Thermostar GDS301 T3). The gas line between the TG and MS was heated to  $200^{\circ}\text{C}$  in order to avoid cold points and thus preventing the condensation of some of the gaseous products. The mass/charge ratios ( $m/z$ ) 44 and 16 were assigned, respectively, to  $\text{CO}_2$  and  $\text{CH}_4$ , respectively.

The higher heating value (HHV) of solid samples was measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) fitted with continuous temperature recording. HTC biochar samples of 0.4–0.5 g were dried at  $105^{\circ}\text{C}$  for 24 h prior to analysis. Results are reported on a dry, ash-free (daf) basis.

Surface morphology studies were carried out by scanning electron microscopy with coupled X-Ray Electron dispersion (SEM–EDX, Quanta 3D FEG, FEI). The samples were prepared by depositing about 50 mg of sample on an aluminum stud covered with conductive adhesive carbon tapes, and then coated with Rh-Pd for 1 min to prevent charging during observations. Imaging was done in the high vacuum mode at an accelerating voltage of 30 kV, using secondary electrons under high vacuum conditions.

The surface chemistry of the hydrochars was studied by FTIR spectroscopy. FTIR spectra were recorded with a PerkinElmer model Paragon 1000 PC spectrophotometer, using the KBr disc method, with a resolution of  $4\text{ cm}^{-1}$  and 100 scans.

### 3. Discussion of results

#### 3.1 HC characterization and thermal degradation study

**Table 1** lists the elemental and proximate analysis of the HCs, as well as the corresponding SY and HHV values.

Two dissimilar HC behaviors were identified from the immediate analyses. On the one hand, one can find HCs with volatile content higher than 85%, indicative of negligible HTC and, on the other hand, samples in which the process readily took place and brought up a clear decrease on volatile matter, with fixed carbon values higher than 50%. Dehydration and decarboxylation are well-known HTC mechanisms, bringing up an expected decrease in moisture and volatile matter content. From our results, both effects are clear although the prominence of them is clearly affected by the experimental conditions; as previously suggested, it seems that there is a cutting point that delimitates when HTC is really taking place. Moreover, it seems that this cutting point is determined by the temperature, whereas time has a slight influence and the biomass/water ratio does not have an effect on its location.

According to the bibliography, biomass starts its decomposition in the presence of water, only when particular subcritical conditions are reached, and water behaves as a non-polar solvent and can therefore make biomass constituents become soluble [11]. Under these conditions, the properties of water such as the ionic constant readily change (it has been reported as being nearly two orders of magnitude higher than at room temperature) [12]. The temperature and pressure defining these conditions is controversial and has been reported as low as  $170^{\circ}\text{C}$  [13] or as high as  $220^{\circ}\text{C}$  [14].

No. run	Ratio % (g/100 ml)	T (°C)	t (h)	SY (%)	Moisture (%)	Vol. (%)	Fixed carbon (%)	Ash (%)	HHV (MJ/kg)
Raw	—	—	—	—	8.9	88.72	1.75	0.63	17.0
1	11.7	200	0.9	93.96	1.62	91.77	5.44	1.17	16.99
2	3.3	230	15.0	29.89	3.51	43.5	52.4	0.57	27.06
3	20.0	170	4.5	95.63	6.91	88.31	4.32	0.46	16.99
4	11.7	150	9.8	93.45	7.6	90.02	1.81	0.57	17.34
5	3.3	170	4.5	94.98	4.84	91.9	1.69	1.57	17.04
6	3.3	230	4.5	21.72	3.31	49.42	49.96	3.31	25.89
7	3.3	170	15.0	59.73	2.61	86.18	6.91	4.31	17.30
8	20.0	170	15.0	83.08	2.88	89.54	7.09	0.49	16.99
9	25.7	200	9.8	49.47	1.92	47.50	52.5	0.49	26.13
10	11.7	200	9.8	44.25	0.22	46.36	51.43	1.99	26.42
11	20.0	230	4.5	46.99	2.59	49.03	44.78	3.74	26.25
12	20.0	230	15.0	47.80	2.44	43.94	50.81	2.81	27.39
13	11.7	200	18.6	44.66	2.73	47.89	47.71	1.68	26.65
14	11.7	200	9.8	44.29	1.57	49.91	44.78	3.74	26.72
15	1.5	200	9.8	42.02	1.65	46.52	51.83	1.65	26.38

**Table 1.**

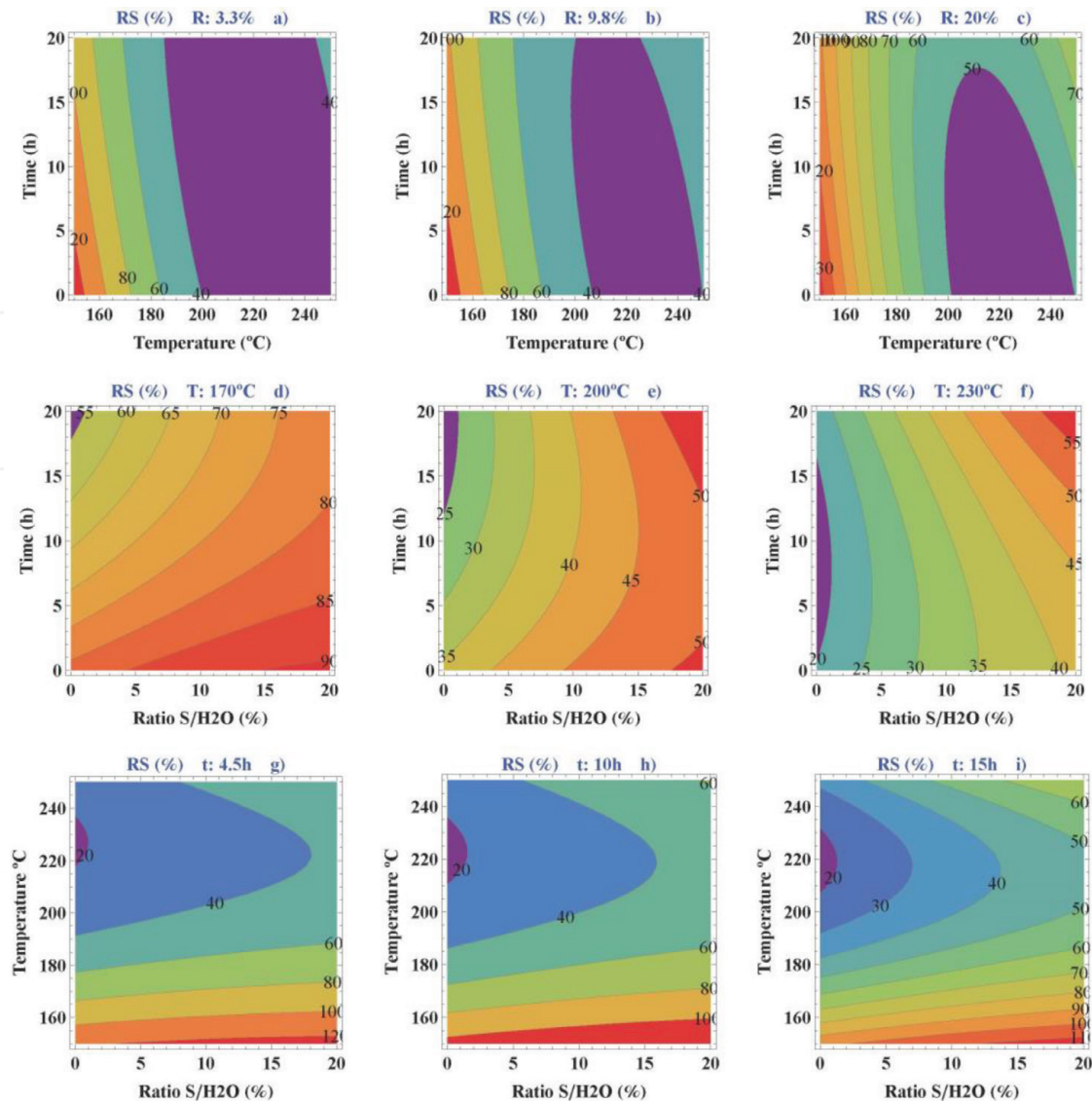
Values for solid yield (SY, %), proximate analysis (%) and high heating value (HHV) (kJ/kg), for reactions made under different Ratio (%), temperature (T), time (t).

The interpretation of the results showed in **Table 1** can be facilitated by plotting 2D level curves for a fixed value of one variable. As an example, **Figure 1** shows these plots for fixed biomass/water ratios (a–c), fixed temperature values (d–f) and fixed time periods (g–i), when the output function is the solid yield (%). A glance to these figures can provide valuable information not only about the effect of the experimental variables but also on their interactions, as it is explained next.

First, it can be observed that for a fixed ratio, increasing temperature involves a lower SY, up to a cutting point for which the process is reversed; this suggests, in coherence with results reported by other researchers, that the presence of reactions responsible for the formation of aggregates from monomers in the liquid phase, that finally migrate to the solid phase might be only possible if a certain temperature is used. Funke et al. [15] identify this effect with the reach of a critical saturation concentration, by which the cellulose fragments (produced from dehydration or decarboxylation, both endothermal processes) react to form cross-linked hydrophobic polymer structures. It is also interesting to notice that this effect is mitigated when a greater ratio is used; probably because of diffusion restrictions. Dissimilarly, for a fixed ratio, time has a scant influence under these conditions.

On the other hand, one can see that for a fixed temperature increasing **R** brings out an increase on the solid yield. Besides, time has a positive influence on the solid yield only if the fixed temperature is low, whereas the tendency is inverted if a high temperature is employed.

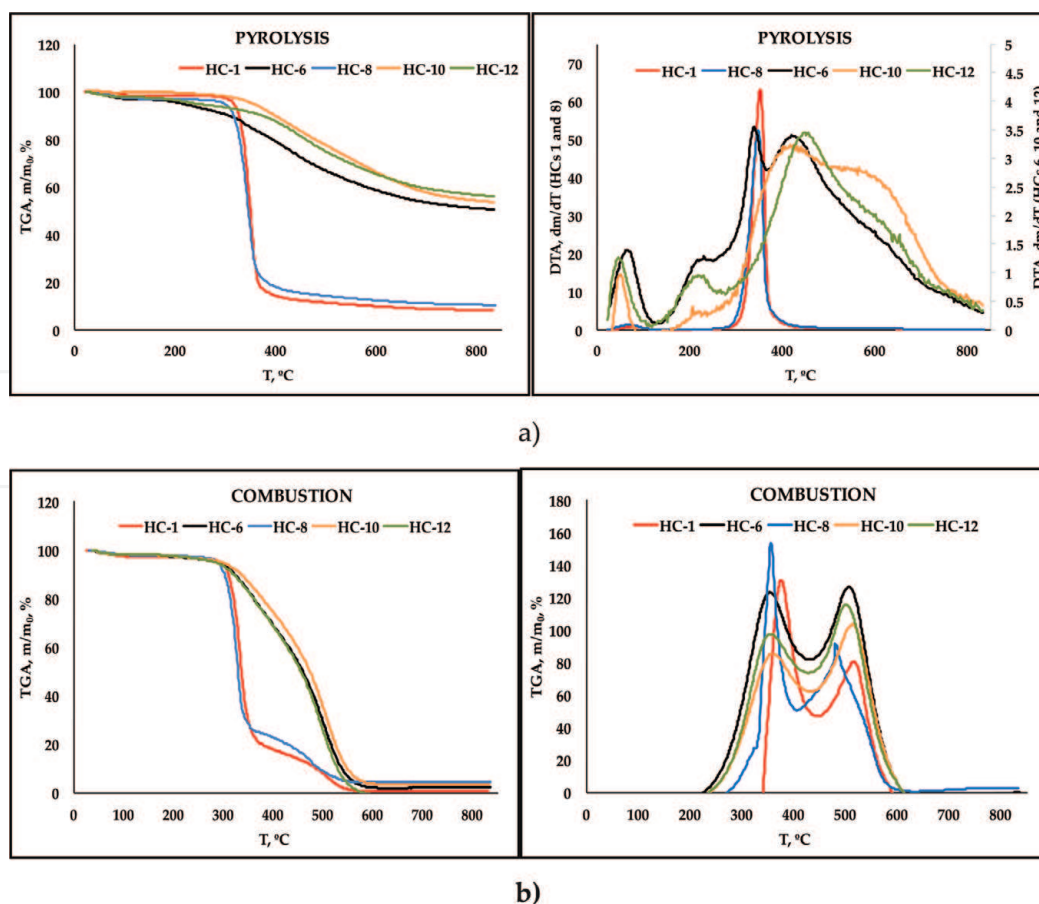
If **t** is fixed, a higher **T** decreases the solid yield, up to a maximum value of SY; thereafter, if **T** is increased, the SY is also enhanced. This temperature value is always higher than 200°C, and decreases for longer treatments. The ratio has a scant influence on the SY for low temperatures and a positive effect on it a higher temperatures.



**Figure 1.** Level curves for solid yield corresponding to HTC processes under varying experimental conditions.

**Figure 2a** and **b** depicts the results obtained from the thermal degradation studies under inert and oxidizing atmosphere, respectively. As it can be inferred from this figure, the first weight loss, associated to moisture, is in general less marked for samples that were hydrocarbonized under more aggressive conditions (and, in all cases, lower than for pure cellulose, see **Table 1**; moisture content of 8.9%), which confirms that HTC was effective as drying process. Hydrolysis and dehydration are, as previously reported, specially favored for higher temperatures. Further on, one can see that the slope of the thermogram step associated to the release of volatile matter is also markedly affected by the experimental conditions. While most of the volatile matter has been degraded for HCs prepared at  $T > 200^{\circ}\text{C}$ , the runs made under soft conditions show TG profiles that almost overlap with that of pure cellulose. This behavior has a clear effect on the fixed carbon content, as explained above.

The breaking-up of volatile matter as a result of HTC has been associated to hydrolysis, dehydration, decarboxylation, decarbonylation or demethanation reactions. Besides, some other reactions responsible for the stabilization (and even further creation) of the solid phase have also been reported (namely condensation, polymerization, and aromatization). By having a look to DTG profiles obtained for biomass precursors [14], one could suggest that the higher proportion of lignin in the HCs prepared under more aggressive conditions is responsible for



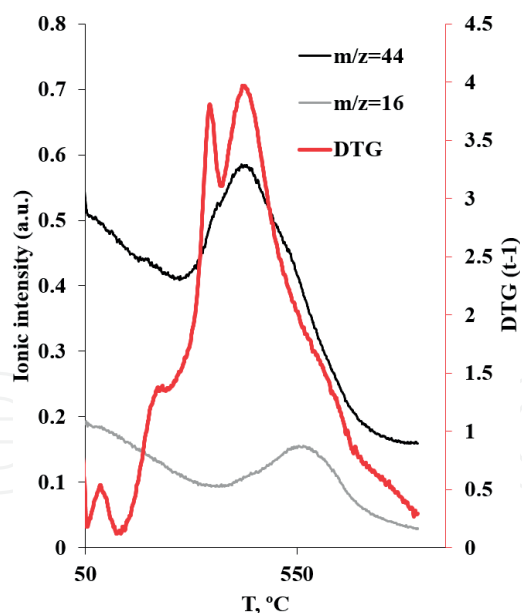
**Figure 2.** Thermal degradation study (TG and DTA) under inert (a) and oxidizing (b) conditions.

the gradual mass release at high temperatures during TGA analyses. However, in the case of cellulose, the examination of DTA curves at temperatures higher than 400°C allows concluding that after effective HTC (samples 6, 10 and 12) a solid phase has been created on the HC, which is more resistant than the precursor. This new constituent accounts approximately for 50% of the HC weight, and degrades in the range of temperature 400–750°C, a temperature range that is associated to *charring* processes [16]. The same trend can be observed from combustion profiles.

Monitoring the emissions associated to thermal degradation processes can be very useful to confirm the prominence of particular reactions pathways. In this work, the emissions associated to the combustion of selected HCs were studied, and, as an example, **Figure 3** shows the ion intensity profiles found for sample 6, made under aggressive conditions (i.e., under which HTC readily took place). The analysis confirms the release of CO<sub>2</sub> along the temperature range associated to the removal of volatile matter, and also, although in a lower extent, at higher temperatures. This in turn is coherent to the existence a fraction of HC that is more resistant to degradation, even under oxidizing conditions, and is the consequence of the aromatization reactions and repolymerization of cellulose fragments, as described previously. CH<sub>4</sub> release is also found at temperatures higher than 500°C, supporting the previous behavior.

### 3.2 HC characterization and thermal degradation study

The surface morphology of the samples was examined by SEM micrography. For the sake of brevity, only some of them have been included in this work, and have been collected in **Figure 4**, classified in two groups in **Figure 4a–e**.



**Figure 3.**  
*Emissions associated to the thermal degradation of HC-6.*

Firstly, one can observe that for sample 1 (a, representative of very mild conditions), the HC surface is smooth and there is presence of some irregular aggregates, which might be associated to the initial steps of cellulose dilution, although the precursor fibrous structure remains almost unchanged. Sample 8 (b), also prepared at low temperature, also exhibited these features.

In contrast, the appearance of samples prepared at temperatures higher than 200°C (such as 6, 10 and 12) is markedly different (**Figure 4c–e**). In these HCs, the surface appears heterogeneous and covered of microspheres of various sizes. The formation of these spheres has been traditionally associated to the breaking-up of cellulose molecules, as found in biomass materials. As a result of hydrolysis, cellulose breaks into small-chain polymers and monomers which further can polymerize as higher molecular weight compounds (is a second solid phase, as it was previously suggested from TG profiles). After hydrolysis (or simultaneously), dehydration is assumed to take place [14]; this process can be both physical (reject of water from the solid precursor) and chemical (removal of hydroxyl groups). The spherical configuration is related to their limited solubility and hydrophobicity, as it minimizes the interfacial surface HC-solvent [17].

The changes induced on the surface chemistry of the HCs were also dependent on the preparation conditions, and, as in the case of the previous analyses, two different trends were found, as a result of a less or more aggressive treatment. **Figure 5** collects the spectra obtained for selected HCs; the assignation of bands was made using suitable bibliography.

As inferred from **Figure 4**, the bands found for HCs 1 and 8 are significantly different in size and location to those found for samples 6, 10 and 12.

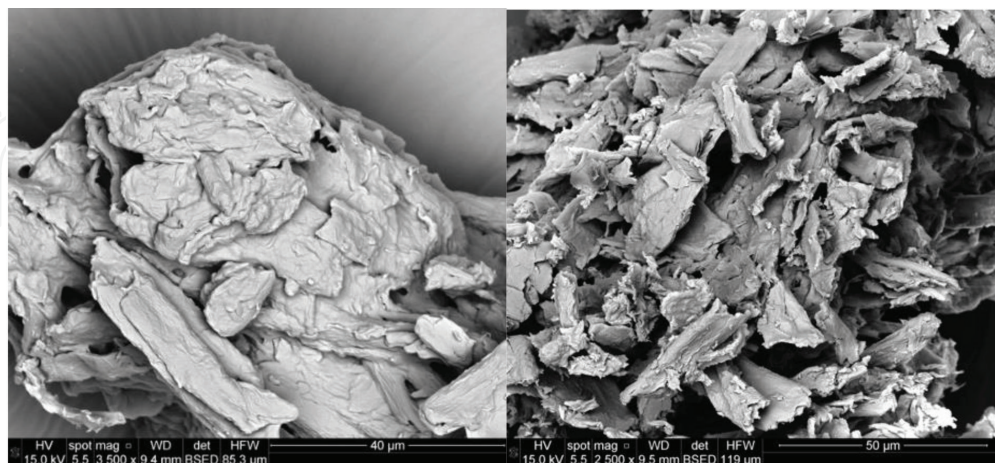
In the first place, the bands usually assigned to –OH groups (signals around 3400 and 2800  $\text{cm}^{-1}$ ) are significantly less intense for those samples hydrocarbonized at higher temperature, suggesting that hydrolysis and dehydration were more prominent in these cases.

Also, as the HTC temperature is increased there is a decrease on the oxygenated groups present on the HC surface; for instance, the vanishing of the spectral band at 1030  $\text{cm}^{-1}$  suggests the removal of ether-type functional groups (C–O).

A peak at 1264  $\text{cm}^{-1}$ , corresponding to the C–O–C bond of cellulose, is clearly found in samples 1 and 8, and remains, also slighter, for the remaining samples, indicating that part of the cellulose was degraded, but there is still a fraction of it that did not react.

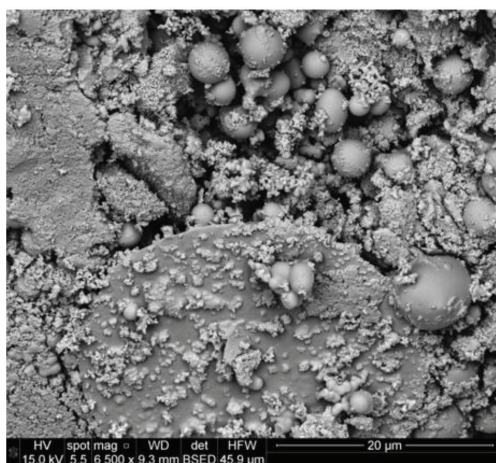


On the other hand, the bands around  $600\text{ cm}^{-1}$  are also less intense. Likewise, other bands appear or become more intense, such as the one located at  $1700\text{ cm}^{-1}$ , suggesting a larger presence of carbonyl groups. Also, the presence of the band at  $1600\text{ cm}^{-1}$  can be associated to a greater aromatization degree (vibration C=C) on the hydrochars.

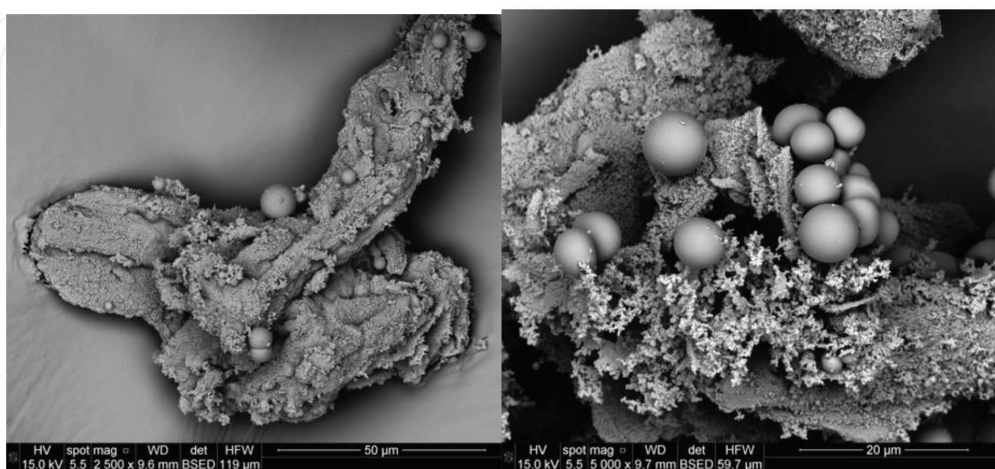


a)

b)



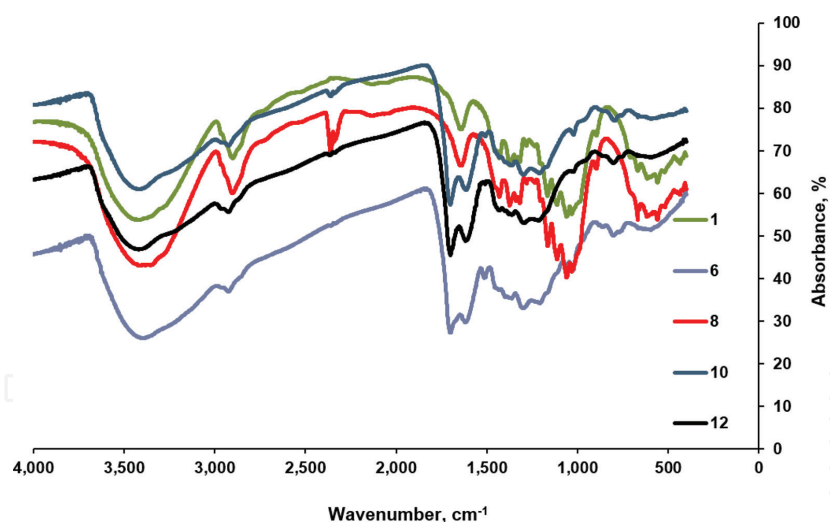
c)



d)

e)

**Figure 4.**  
SEM micrographs of selected HCs: (a) 1 (magnification: 3500); (b) 8 (magnification: 2500); (c) 6 (magnification: 6500); (d) 10 (magnification: 2500); and (e) 12 (magnification: 5000).



**Figure 5.**  
*FT-IR spectra of selected hydrochars.*

#### 4. Concluding remarks

The HTC of cellulose brings out a significant amount on the physical and chemical features of the material, that, depending on the experimental conditions used, can be determinant for its further use.

It was found that there is a lower limit in the experimental reaction conditions that has to be attained in order to guarantee that HTC takes place and that, in the case of cellulose, this point is associated to the use of temperatures higher than 200°C. Once these conditions are reached, the prominence of a complex combination of reactions takes place (hydrolysis, dehydration, decarboxylation, decarbonylation, repolymerization, condensation, aromatization...), whose occurrence gives rise to significant changes on the HC chemical composition, morphology, and surface functional groups.

Apart from the increase in fixed carbon and decrease in volatile matter and moisture (and, in consequence, enhanced energy densification), the behavior towards pyrolysis and combustion is clearly modified after HTC. In this way, it is confirmed that the fragments resultant from cellulose breaking are combined and a new solid is formed, with lignite-type features, and enhanced resistance to thermal degradation. The release of CO<sub>2</sub> during combustion can confirm this effect, since it was present upon degradation up to temperatures as high as 700°C.

Other important features brought up by HTC are related to the different surface morphology, increase in aromaticity, hydrophobicity and development of oxygen surface groups, whose abundancy can also be modeled as a result of the experimental conditions.

These changes justify the use of HTC as sustainable and straightforward method to produce materials suitable for many applications, and also as pretreatment for other processes. The lower moisture is advantageous for improving storage conditions, and also to avoid cost-intensive drying processes prior to combustion processes. Also, the enhanced heating value and hydrophobicity is positive for the use of HCs as biofuels.

The greater porosity and stability provide a better behavior towards applications related to soil remediation and adsorption processes. Besides, the availability of  $\pi$  electrons related to greater aromaticity is very interesting if the HC is to be used to produce supercapacitors or other energy storage devices.

Finally, the variety and abundance of oxygenated functional groups is related to an enhanced reactivity towards activation and improved adsorption performance towards particular adsorbates.

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