

Article

A Sustainable Approach on Spruce Bark Waste Valorization through Hydrothermal Conversion

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Abstract: In the context of sustainable use of resources, hydrothermal conversion of biomass has received increased consideration. As well, the hydrochar (the solid C-rich phase that occurs after the process) has caused great interest. In this work, spruce bark (*Picea abies*) wastes were considered as feedstock and the influence of hydrothermal process parameters (temperature, reaction time, and biomass to water ratio) on the conversion degree has been studied. Using the response surface methodology and MiniTab software, the process parameters were set up and showed that temperature was the significant factor influencing the conversion, while residence time and the solid-to-liquid ratio had a low influence. Furthermore, the chemical (proximate and ultimate analysis), structural (Fourier-transform infrared spectroscopy, scanning electron microscopy) and thermal properties (thermogravimetric analysis) of feedstock and hydrochar were analyzed. Hydrochar obtained at 280 °C, 1 h processing time, and 1/5 solid-to-liquid ratio presented a hydrophobic character, numerous functional groups, a lower O and H content, and an improved C matter, as well as a good thermal stability. Alongside the structural features, these characteristics endorsed this waste-based product for applications other than those already known as a heat source.

Keywords: spruce bark; waste; hydrothermal conversion; hydrochar; characterization



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1. Introduction

Following the development trend of the worldwide industry, there is no activity that does not generate recyclable materials. The increasingly pressing demand of society to move towards the circular economy models drives the scientific community to explore new routes to fully valorise wastes in order to achieve the zero-waste objective [1]. From this perspective, all the residues of industrial processing must not be considered as wastes, the disposal of which involves costs, but rather they should be seen as resources. In particular, in Europe the wood processing activities produce a large amount of residues: for example, the European production of biomass wastes achieves 2.6 million tons per year, which correspond to 237.210 tons of reusable residues per year [2].

Therefore, this large amount of waste requires sustainable exploitation, which can consist in extractions of valuable compounds [1,3–6] or in biochemical or thermochemical conversion routes.

A biocascading approach [1] allows for collecting interesting compounds, but also produces ultimate products, which, with the purpose to keep it into the circular economy loop, can be differently valorised.

Literature reported several thermochemical methods for conversion of lignocellulosic waste into high-added value products: torrefaction, hydrothermal conversion, pyrolysis, and gasification [7–9]. Pyrolysis process can be conducted as both fast and slow pyrolysis. The first, occurs at higher temperatures (500–1000 °C) with a small residence time, and is more orientated to bio-oil production, while slow pyrolysis presents similar yield of bio-oil, valuable gases, and biochar [10] and occurs at 300–700 °C during several hours [11]. Although pyrolysis has several advantages (the possibility of using various types of biomass, reasonable product distribution, good yields) this type of conversion still has some drawbacks, such as the feedstock requires drying before conversion, which leads to higher energy consumption as well higher production costs [12].

Torrefaction is considered a conventional thermal pre-treatment to improve physical-chemical properties of biomass [13]. During torrefaction biomass is heated in an inert atmosphere up to 200–350 °C for 30 min up to several hours. If a biomass with high content of moisture is not suitable for torrefaction, a pre-drying process being recommended [14]. Gasification converts biomass into a gas blend (carbon dioxide, carbon monoxide, and hydrogen) by reacting the feedstock at high temperatures (>700 °C), very short residence time (10–20 s), with a controlled amount of oxygen and/or steam, and very good conversion yields (around 85%) [15].

The hydrothermal conversion process (HTC) is an efficient technique for biomass conversion to valuable rich carbon materials. During HTC, the feedstock is converted into a homogenous lignite-like material [16,17] in a closed system under mild temperature (150–280 °C) with self-generated pressure [18,19]. The main advantage of the HTC process is the use of undried raw biomass, which leads to a lower production cost. Subsequently, the water present in the feedstock will act as a solvent and catalyst in the process, facilitating the hydrolysis reaction and the decomposition of lignocellulosic components [20]. Up to date, the HTC have been carried out on different type of biomass, such as food waste [21–24], olive mill wastes [25], sewage sludge [26–31], digested agro-industrial sludge [32], grape pomace [33], cellulose [34–36], holocellulose [37], lignin [38], spent coffee ground [39], tobacco stalk [40], corn stalk [41], corn stover [42], and wood biomass: pinewood sawdust [43], eucalyptus bark [44], nut shell [45,46], walnut shells [33], wood chips from pine and different logging residues [47], beech wood chips [36], pine wood meal [48], macadamia nut shell [46], coffee wood and *Eucalyptus* sp. wood [49], and Japanese cedar [50].

The resulted high carbon rich solid product is hydrochar (HC) and its properties highly depend on the process parameters: reaction temperature, residence time, and biomass to solvent ratio. For this reason, a systematic process study is critical. Hydrochar produced by hydrothermal conversion of biomass have been traditionally used as a heat source, adsorbent, and catalyst support. Recently, this carbonaceous material is viewed as a precursor for activated carbon with tailored characteristics [51] and consequently, with various applications in energy storage, environmental remediation and resource recovery, or even in the medical field [15,52].

This study is focused on spruce bark (*Picea abies*) decomposition through a hydrothermal process with the main goals: (i) to produce hydrochar from spruce bark (SB) wastes, (ii) to study the process and highlight the relevant influence of process parameters, (iii) to reveal the chemical, structural, and thermal characteristics of the HC in order to prove the use of this material as a reactive filler in composite design [53,54]. To the best of our knowledge, none of these aspects have been studied before.

2. Materials and Methods

2.1. Materials

The biomass used in this study was spruce bark that resulted in large quantity from eastern European countries as waste from forestry and wood processing. In the first step, the feedstock was dried at room temperature under aeration conditions and ground in a Grindomix GM 2000 laboratory mill to a particle size distribution between 0.5–1.5 mm, then stored in an airtight container protected from moisture.

Throughout the study, chemicals and reactive agents of analytical purity provided by Sigma-Aldrich (Merck KGaA, Darmstadt, Germany) were used: toluene, ethyl alcohol, sulfuric acid 96%, nitric acid 65%, acetic acid, petroleum ether, acetone, and potassium hydroxide.

2.2. Methods

2.2.1. Hydrothermal Process Study

The HTC of SB was conducted in a stainless-steel autoclave, with 2 L glass vessel inside equipped with a drain valve, manometer, and a temperature sensor (Figure 1). For each run, 120 mg of spruce bark was dispersed in 600 or 1200 mL of deionized water in order to reach 1/5 and 1/10 solid-to-liquid ratio, and then placed into the autoclave.

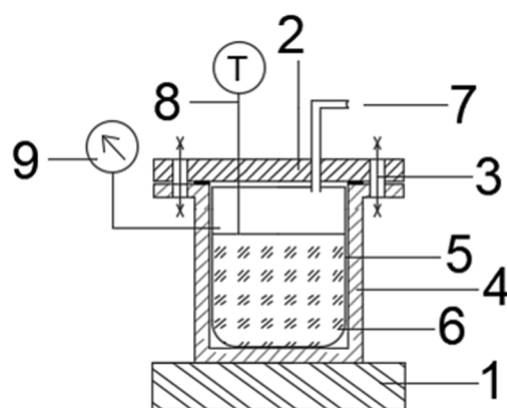


Figure 1. The HTC apparatus: 1 source of heat; 2 autoclave cover; 3 screws; 4 stainless steel autoclave; 5 glass vessel; 6 spruce bark and deionized water; 7 drain valve; 8 temperature sensor; 9 manometer.

The reactor was tightened closed and heated at a temperature of 200, 240, and 280 °C for 1, 2.5, and 5 h, respectively. After HTC process, the stainless steel autoclave was cooled down at room temperature, providing sufficient time for autoclave depressurization. The mixture inside of the reactor was subjected to filtration, in order to separate the hydrochar from the liquid phase. The solid phase was washed with deionized water until the yellow-brown coloration of the wash waters was no longer observed. The liquid phase was stored at 3 °C for the next characterization. Hydrochar was dried at 105 ± 3 °C until a constant mass is reached, then it was weighed and stored in a closed container for further characterization and uses. The samples were labelled as SB for the feedstock and HC-200, HC-240, and HC-280 for the hydrochar obtained according to the temperature used during the process. All experiments were made in triplicate and the mean value was reported. The yield in hydrochar (Equation (1)) and the spruce bark conversion degree (Equation (2)) were calculated as follow:

$$\text{Yield} = \frac{M_{\text{HC}}}{M_i} \times 100\% \quad (1)$$

$$\text{Conversion degree} = \frac{M_i - M_{\text{HC}}}{M_i} \times 100\% \quad (2)$$

where M_{HC} is the mass of hydrochar (g), M_i is the mass of initial feedstock (g).

2.2.2. Experimental Design and Statistical Analysis

In order to determine the influence of independent variables on the dependent variables in a regression study, the ANOVA test was performed. A response surface methodology (RSM) by means of central composite design was used to fit the conversion degree response as a function of three factors: temperature, residence time, and solid-to-liquid ratio.

A complete experimental planning (2×3^2) with three factors was proposed in order to study the thermochemical conversion of SB, as well as to obtain the highest conversion degree. Temperature (°C) and residence time (h) were followed for three levels, while

solid-to-liquid ratio (w/v) was considered on two. Statistical analysis was performed using the MiniTab software 17.1.0.

The experimental results of the response surface design were analyzed and p -values less or equal with 0.001 were considered to be statistically significant. All experiments were conducted in triplicate, and the average of each set of experiments were related in Table 1.

Table 1. The conversion degree of SB according to experimental design.

No. Exp.	Solid-to-Liquid Ratio (w/v)	Temperature ($^{\circ}\text{C}$)	Residence Time (h)	Conversion Degree (%)
1	1/5	200	1.0	25.24 ± 1.46
2	1/10	200	1.0	26.81 ± 0.72
3	1/5	240	1.0	29.60 ± 0.58
4	1/10	240	1.0	32.01 ± 0.41
5	1/5	280	1.0	42.59 ± 1.48
6	1/10	280	1.0	45.03 ± 0.46
7	1/5	200	2.5	26.71 ± 0.45
8	1/10	200	2.5	29.80 ± 0.53
9	1/5	240	2.5	32.82 ± 0.14
10	1/10	240	2.5	33.19 ± 0.61
11	1/5	280	2.5	43.19 ± 0.74
12	1/10	280	2.5	45.12 ± 0.29
13	1/5	200	5.0	24.48 ± 1.29
14	1/10	200	5.0	27.19 ± 0.67
15	1/5	240	5.0	36.03 ± 0.76
16	1/10	240	5.0	36.96 ± 0.33
17	1/5	280	5.0	43.32 ± 0.70
18	1/10	280	5.0	45.01 ± 0.80

2.2.3. Characterization Methods

Both SB and HC followed a proximate and ultimate analyses in order to relieve the general chemical profile of samples. The laboratory analytical procedures for standard biomass analysis (NREL) were applied for SB and HC characterization [55–58]. For the determination of moisture content, samples were dried in a BINDER oven at $105 \pm 3^{\circ}\text{C}$, while the ash content analysis was carried out in a Nabertherm oven at 600°C .

In order to set out the hemicellulose, cellulose, and lignin content, the biomass was subjected to conventional methods: the cellulose was dosed by the nitro-alcoholic method [59], while the Klason-Komarov protocol [60] was followed for the lignin content.

The morphology of the samples was studied by scanning electron microscopy (SEM) using a Carl Zeiss SMT FESEM-FIB (Scanning Microscope Tunneling Field Emission Scanning Electron Microscope-Focused Ion Beam) Auriga, Oberkochen, Germany, equipped with an EDX elemental analysis system. SEM studies were performed on uncovered samples fixed on platinum-coated supports.

The IR spectra of both SB and HC were performed using a PerkinElmer Spectrum 100 FTIR spectrophotometer in attenuated total reflection mode (ATR-FTIR) using 4 cm^{-1} resolution and 15 scans. The FT-IR spectra were collected between 4000 cm^{-1} and 500 cm^{-1} in transmittance mode. All determinations were performed at room temperature.

The specific surface area was determined through BET method, based on nitrogen adsorption using an Autosorb 1 MP (Quantachrome, Boynton Beach, FL, USA) analyser.

The thermal properties of both SB and HC were studied by thermogravimetric analysis in nitrogen atmosphere, in a temperature range of 25 °C to 700 °C with a 10 K min^{−1} constant heating rate and 40 mL min^{−1} nitrogen flow using a Mettler Toledo TGA-SDTA851 equipment. The samples weight subjected to analysis were between 2.57 mg and 4.95 mg. The results were expressed through thermogravimetric (TG) and differential thermogravimetric (DTG) curves, respectively.

3. Results and Discussion

3.1. Experimental Design and Process Study on Spruce Bark HTC

According to the literature, the HTC is efficient at temperatures between 180–300 °C with residence time from 30 min to several hours with autogenous pressure [15,61–64]. In order to study the hydrothermal conversion of spruce bark and to highlight the main parameters influence, we conducted our experiments in the temperature range of 200 °C to 280 °C, the residence time from 1 to 5 h, with a solid-to-liquid ratio of 1/5 and 1/10.

The dependent (output) parameter was considered as the conversion rate expressed in percentage. As experimental design, a complete factorial model of 2×3^2 was chosen, in which one parameter (solid-to-liquid ratio) was on two levels, while temperature and residence time were on three levels (Table 2).

Table 2. The input parameters levels.

No. crt.	Input Parameters	Unit	Level	Value
1	Solid-to-liquid ratio	(w/v)	−1	1/5
			1	1/10
2	Temperature	°C	−1	200
			0	240
			1	280
3	Residence Time	h	−1	1.0
			0	2.5
			1	5.0

As each run was repeated three times, the experimental design comprised of 54 experiments. Table 1 revealed the data, where the mean value and the dispersion (by the mean square deviation) was calculated for each group of three experimental data. The maximum dispersion was 1.48, and the minimum 0.14.

The conversion degree was considered to be the most important quantitative index, which reflected how much spruce bark was converted into hydrochar during HTC.

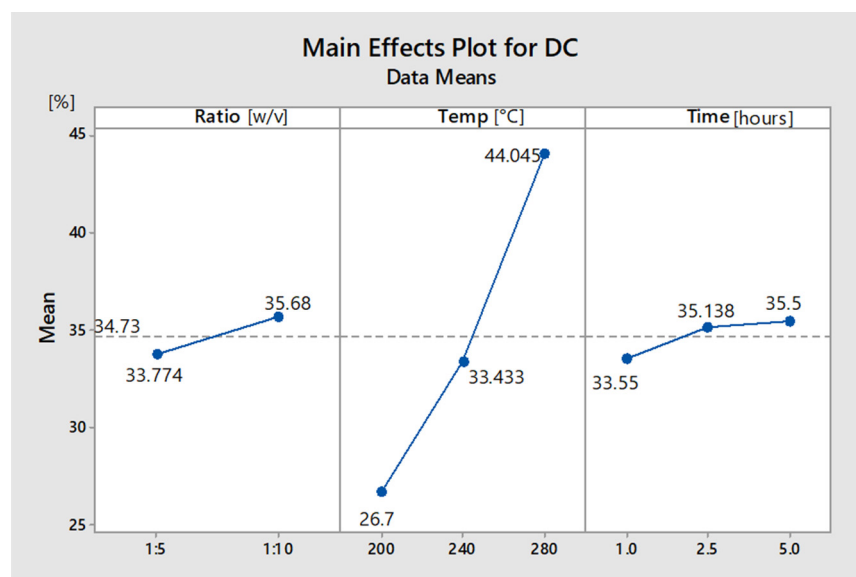
For statistical analysis of experimental data, a MiniTab software was used. The analysis of variance (ANOVA method) allowed the hierarchy of the independent parameters on the conversion degree (Table 3). It had been observed that all factors exerted a statistically significant influence ($p \leq 0.001$). However, temperature had the greatest influence on the conversion degree (test value $F = 582.76$) and could be considered the dominant parameters on conversion degree, followed by the solid-to-liquid ratio ($F = 20.78$) and the residence time ($F = 8.21$).

Table 3. The ANOVA variance analysis.

Source	DF *	Adj SS	Adj MS	F-Value	p-Value
Solid-to-Liquid Ratio	1	49.05	49.05	20.78	<0.001
Temperature	2	2751.83	1375.92	582.76	<0.001
Residence Time	2	38.77	19.39	8.21	0.001
Error	48	113.33	2.36		
Lack-of-Fit	12	91.32	7.61	12.45	<0.001
Pure Error	36	22.01	0.61		
Total	53	2952.99			

* DF—Degrees of freedom; Adj SS—Adjusted sums of squares; Adj MS—Adjusted mean squares.

Figure 2 highlighted the influence of the three independent parameters with a direct influence on the conversion degree. The increase of their value leads to the increase of the conversion degree. Thus, as the temperature rises in the range of 200–240 °C, the conversion degree increases slowly, whereas an increase in temperature in the range of 240–280 °C causes a considerable enhancement of conversion degree. In terms of residence time, the conversion degree is relatively similar in the range of 1–2.5 h and the range of 2.5–5 h.

**Figure 2.** The influence of independent parameters on the conversion degree.

In order to demonstrate the best parameter levels for HTC of SB, three-dimensional surface plots (Figure 3) were constructed according to the polynomial models. Figure 3 shows the effect of temperature and residence time on the conversion degree of SB, for a solid-to-liquid ratio at 1/5. The conversion degree consistently increased with the increase in temperature. Thus, with the increase of reaction temperature, spruce bark underwent a better break down into hydrochar. Considering the chemical composition of feedstock, which consisted mostly in hemicellulose, cellulose, and lignin, at higher temperatures a substantial amount of main components were subjected to several reactions, which led to a better conversion into hydrochar [65,66].

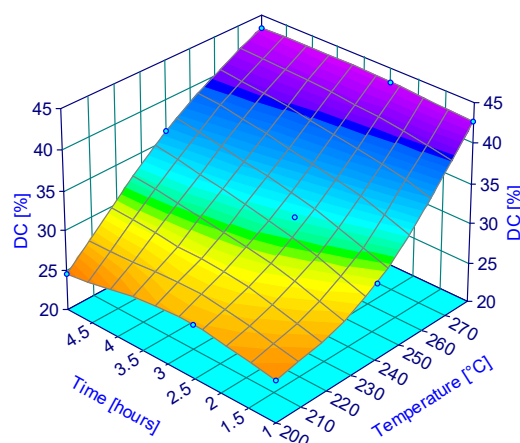


Figure 3. Response surface plot showing the effect of temperature ($^{\circ}\text{C}$) and residence time (h) on the SB conversion degree (solid-to-liquid ratio of 1/5).

The ANOVA tests proved the conversion degree was higher if the temperature was higher. However, even if a higher conversion degree was the goal, we must consider the high pressure generated inside the autoclave during the HTC process. The pressure was considerable up to 280°C , reaching up to 70 atm (Figure 4), and to retain it for hours could be hazardous.

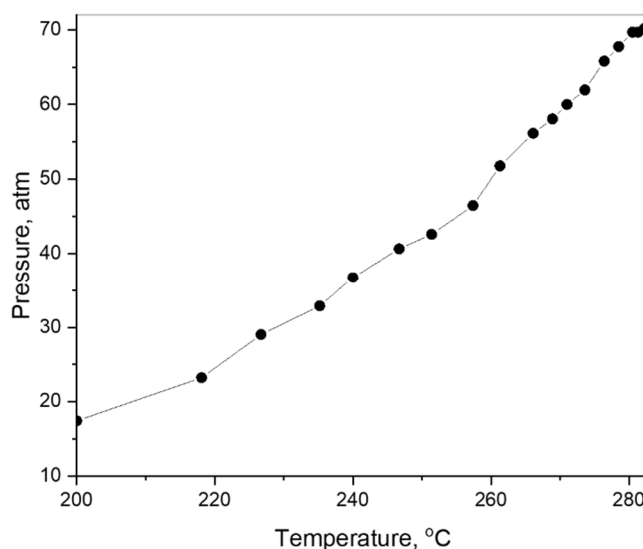


Figure 4. Pressure of saturated water vapor as a function of temperature.

For handling the process in a safe and cost-effective mode, a set of reasonable parameters that led to extremely good conversion rates were proposed: the temperature 280°C and the residence time of 1 h. Considering that the solid-to-liquid ratio had a low influence on the conversion degree and with the intention to reduce consumption further, the solid-to-liquid ratio was set up to 1/5.

3.2. Proximate and Ultimate Analysis

Proximate and ultimate analysis have been used to characterize the feedstock and hydrochar properties. Proximate analysis is used to obtain an overall composition in terms of main compounds, ash, and moisture content, while the ultimate analysis gives the weight percentages of major elements (C, H, S, O) (Table 4).

Table 4. Main physical and chemical characteristics of spruce bark and hydrochar.

Analysis		Spruce Bark (SB)	Hydrochar (HC-200)	Hydrochar (HC-240)	Hydrochar (HC-280)
Yield, wt.%		-	74.76 ± 1.19	70.40 ± 0.48	57.41 ± 1.21
Proximate Analysis	Moisture, wt.%	8.35 ± 0.30	3.59 ± 0.29	2.46 ± 0.25	1.98 ± 0.30
	Ash, wt.%	2.17 ± 0.30	1.86 ± 0.24	1.03 ± 0.15	0.66 ± 0.14
	Hemicellulose, wt.%	15.42 ± 0.53	-	-	-
	Cellulose, wt.%	31.27 ± 1.01	25.70 ± 0.92	13.80 ± 0.45	2.50 ± 0.25
	Lignin, wt.%	40.48 ± 0.73	40.10 ± 1.18	39.50 ± 1.02	38.46 ± 0.63
Ultimate Analysis	Carbon, wt.%	58.26	60.13	62.80	71.61
	Hydrogen, wt.%	5.84	5.70	5.44	5.20
	Oxygen, wt.%	33.15	28.14	25.12	21.11
	Magnesium, wt.%	0.05	0.02	-	-
	Aluminium, wt.%	0.01	-	-	-
	Silicon, wt.%	0.01	-	-	-
	Phosphorus, wt.%	0.04	-	-	-
	Sulphur, wt.%	0.05	-	-	-
	Chlorine, wt.%	0.01	-	-	-
	Potassium, wt.%	0.33	0.10	-	-
	Calcium, wt.%	1.59	1.52	1.49	1.44
	Manganese, wt.%	0.02	-	-	-
	Copper, wt.%	0.38	0.38	0.38	0.38
	Zinc, wt.%	0.27	0.27	0.26	0.26

HC-200 = HC resulted at 200 °C; HC-240 = HC resulted at 240 °C; HC-280 = HC resulted at 280 °C.

As expected, SB presented a higher moisture and ash content than HC. This aspect is due to the decomposition of hemicellulose, cellulose, and lignin during hydrothermal conversion and to water-soluble elements, such as potassium and calcium that are dissolved in water during the process [67]. Spruce bark is a softwood that contain 15.42% hemicellulose, 31.27% cellulose, and 40.48% lignin. The results obtained for the main components are in accordance with other reported results [68–70]. HC resulted from hydrothermal conversion at 280 °C (HC-280) was subjected to conventional methods in order to highlight the main compounds remaining untransformed after the process. Thus, the HC-280 still contain 2.5% of cellulose, while the percentage of unreacted lignin was 38.46%.

The ultimate analysis showed a change in the elemental composition of samples. The C and O content were significantly modified, with C increased from 58.26% in SB to 71.61% in HC-280, and O decreased from 33.15% in SB to 21.11% in HC-280. The H content decreased slightly from 5.84% in SB to 5.20% in HC-280. Krysanova and co-authors concluded that a decrease of O content was due to dehydration and decarboxylation reactions during the HTC process, where a result of which H₂O and CO₂ are formed [71]. A similar hypothesis was presumed by Wang and co-authors [67] regarding the hydrogen content decrease. Similar behavior of C, O, and H contents were reported by other researchers for wood sawdust, walnut shell, tea stalk, apricot seed, hazelnut husk [45], *Opuntia ficus-indica* [72], wood chips [36], bamboo [16], and pine wood [48].

Some inorganic elements (P, K, S, Cl, Mn, Mg) initially presented in feedstock were no longer found in HC-200 and HC-240, due to the partially or complete dissolution in the liquid phase. After HTC, no traces of Mg, Al, Si, P, S, Cl, and Mn content were found in HC-280.

The first main compound that was subjected to hydrolyzation in HTC was hemicellulose, which started to degrade at temperatures of 200 °C [73]. Although not all the reactions involved in HTC were well known, the general pathways of the main components could be understood. If temperature increased, the volatile compounds were released, increasing carbon content. Furthermore, the temperature increase boosted dehydration reactions, removing oxygen from the initial biomass structure, resulting in a decrease in the O to C ratio [64]. Above 200 °C, the cellulose depolymerisation occurred [74] and according to our data this component was difficult to be completely degraded up to 280 °C, and a small content (2.5%) was still present in HC.

3.3. The Structural Assessment

Figure 5 shows the SEM images on spruce bark and hydrochar and gives information on the morphological structure of samples. On the surface of the spruce bark an uneven particle with a low porosity had been observed. Wang and co-workers reported that in the cell wall of plants, oriented cellulose fibers were interconnected and linked together by disoriented hemicellulose chains [75].

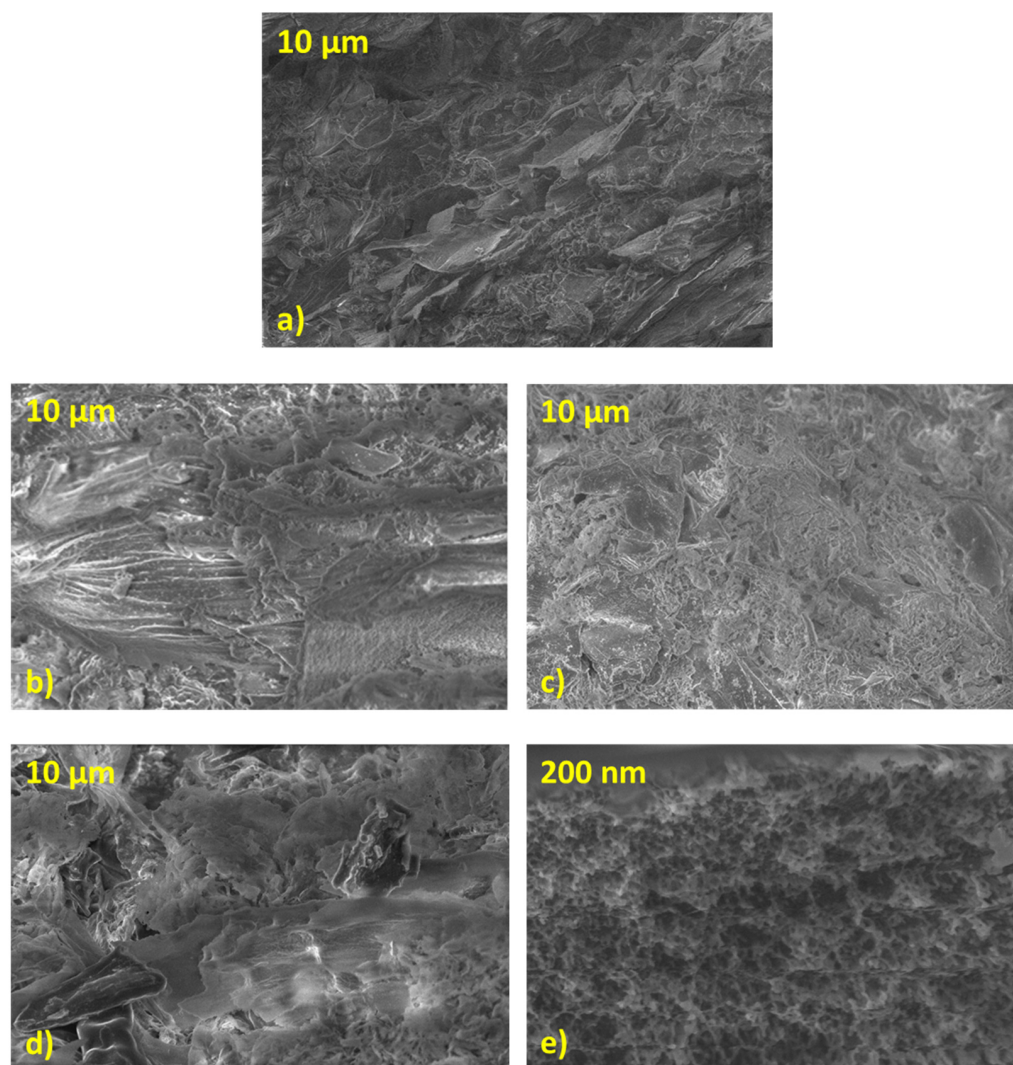


Figure 5. SEM images on SB (a), HC-200 (b), HC-240 (c) and HC-280 (d,e).

The spruce bark had a fibrous structure with high length-to-diameter ratios, that was characteristic for lignocellulosic biomass [44]. The hydrochar obtained from spruce bark at 280 °C had a bark-like skeleton, keeping approximately the same anatomical structure

similar to the feedstock. This aspect could confirm that during the hydrothermal conversion (up to 280 °C) the spruce bark did not suffer a complete degradation. For lower temperature (200 or 240 °C) HC-200 and HC-240 presented a similar anatomical structure with HC-280, and it could be seen that the morphology changes were imperceptible. However, it was observed that HC-280 had a more uniform surface compared to SB, due to the complete conversion of hemicellulose and partial degradation of cellulose and lignin. The textural features of hydrochars were critical in determining their potential application capabilities. In terms of morphology, hydrochars were generally heterogeneous, with a wide range of pore sizes and shapes. This became obvious for HC-280, which exhibited sporadic but well-developed porous areas, as shown in Figure 5. The presence of this porosity was reflected in value of the surface area, highlighted by the BET analysis.

Başakçılardan Kabakcı and Baran reported that the slightly porous structure and uneven distribution of hydrochar obtained from softwoods was due to the hydrolysis reaction of hemicelluloses [45].

3.4. Fourier Transform Infrared Spectroscopy

The FT-IR spectra recorded for spruce bark (SB) and hydrochars (HC-200, HC-240, and HC-280) (Figure 6) had almost the same pattern, indicating similarities in structure and composition. The main functional groups were depicted (Table 5) and data reported in the literature were taken into account as well [40,41,44,76–80].

Table 5. Functional groups of SB, HC-200, HC-240, and HC-280.

Wave Number (cm ^{−1})	Functional Groups	Description	References
3500–3000	O–H	Hydroxyl or carboxylic alcohols of cellulose or phenols of lignin	[40,41,44]
2923	C–H	Stretching vibration of aliphatic C–H	[40,41,44]
2297	C–O	Stretching vibration of aliphatic C–O	[76]
1696	C=O	Carbonyl, ester, or carboxyl from cellulose and lignin	[41,79,80]
1611	C=C	Aromatic skeleton present in lignin	[41,44,78]
1448	C–H	Deformities in lignin and carbohydrates	[40,80]
1264	C–O	Esters of hemicellulose	[40,80]
1148	C–O–C	Vibrations in cellulose and hemicellulose	[41]
1025	C–O	Vibrations in cellulose and lignin	[40,41,44]
870–750	C–H	Aromatic C–H out-of-plane bending vibration	[40,77]

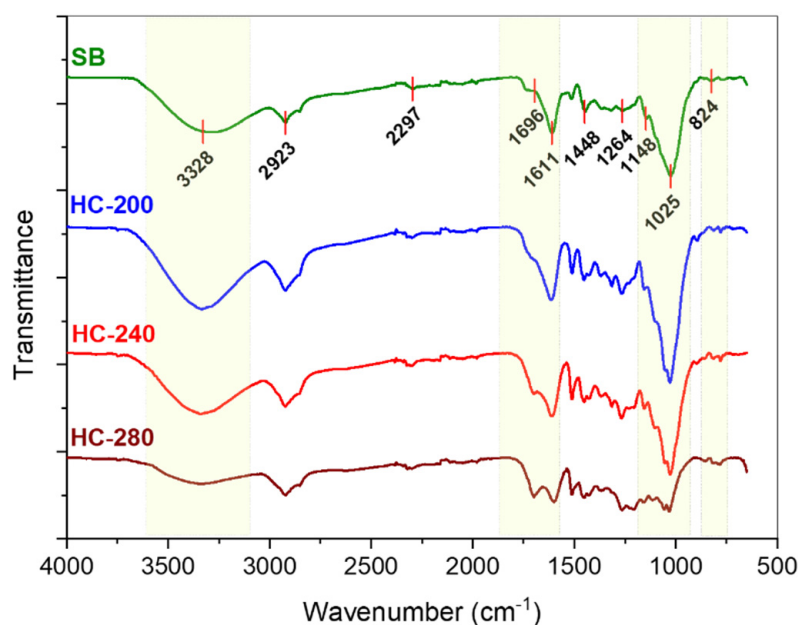


Figure 6. FT-IR spectra of SB, HC-200, HC-240, and HC-280.

The wide band between 3500–3000 cm^{-1} was characteristic to the stretching vibrations of the O–H bonds. The absorption picks in the range of 2923 cm^{-1} and 2297 cm^{-1} indicated the presence of the C–H and C–O bond, respectively, which suggested an aliphatic passage. The absorption band at 1696 cm^{-1} corresponded to the vibration of the C=O bond, thus probably indicated the presence of ketones and/or aldehydes. The shoulder at 1611 cm^{-1} could be attributed to the elongation vibrations of the C=C bonds with aromatic character. The band with the maximum absorption at 1448 cm^{-1} could be assigned to the plane deformation of the C–H bond. The absorption pick at 1025 cm^{-1} indicated the presence of C–O bond vibration. The bands in the range 870–750 cm^{-1} could be attributed to the out-of-plane vibrations of the C–H bonds, in aromatic systems with substituents in different positions of the benzene ring.

However, the HTC process induced structural changes, and some differences in the hydrochar's FT-IR spectra were noticed. The intensity of the 3500–3000 cm^{-1} band decreased with the increase of the process temperature, and this behaviour could be attributed to a dehydration reaction. As the temperature increased, the bands at 1611 cm^{-1} and 1696 cm^{-1} , became wider and stronger. This change suggested that aromatic rings were formed and/or recombined at higher temperatures, a finding also reported by Gao et al. [44].

The band with the maximum absorption at 1448 cm^{-1} could be associated to C–H deformation in lignin and carbohydrates [80–82]. Moreover, the peak at 1318 cm^{-1} became weaker with the increase of temperature. This aspect could be attributed to the decomposition of cellulose/hemicelluloses and to the partial degradation of stable lignin. It was observed that with the increase of the HTC temperature, the intensity of the absorption bands from 1148 cm^{-1} (C–O–C) and 1025 cm^{-1} (C–O) began to decrease, observing the almost complete disappearance of peaks in the case of HC-280. The higher the process temperature, the more parts of cellulose can be destroyed [40].

The appearance of the absorption maximum in the range 870–750 cm^{-1} may possibly be attributed to the aromatization reaction that could have taken place [78].

3.5. Brunauer-Emmett-Teller (BET) Surface Area Analysis

In order to highlight the specific surface area following the BET methodology, a degassing process was performed by heating the samples under vacuum conditions. Subsequently, the samples were cooled and brought to atmospheric pressure by filling them

with nitrogen. Finally, the samples were cooled to $-196\text{ }^{\circ}\text{C}$ under vacuum conditions, thus promoting the adsorption process.

All three adsorption-desorption isotherms of nitrogen (Figure 7) demonstrated the presence of the hysteresis loop, which was closed in the range of relatively low pressures. The BET surface area was between $5\text{--}13\text{ m}^2\cdot\text{g}^{-1}$ and the maximum value was attributed to the hydrochar obtained at $280\text{ }^{\circ}\text{C}$. Micropores volume was determined by V-T method [83,84] and the mesopores volume was determined by the difference between the total volume and the micropores volume. The data listed in Table 6 showed that the increase of temperature led to an improvement of surface area and mesopores volume of hydrochar. A small specific surface area indicated a weak activation of the hydrochar and no traces of micropores were identified in the samples.

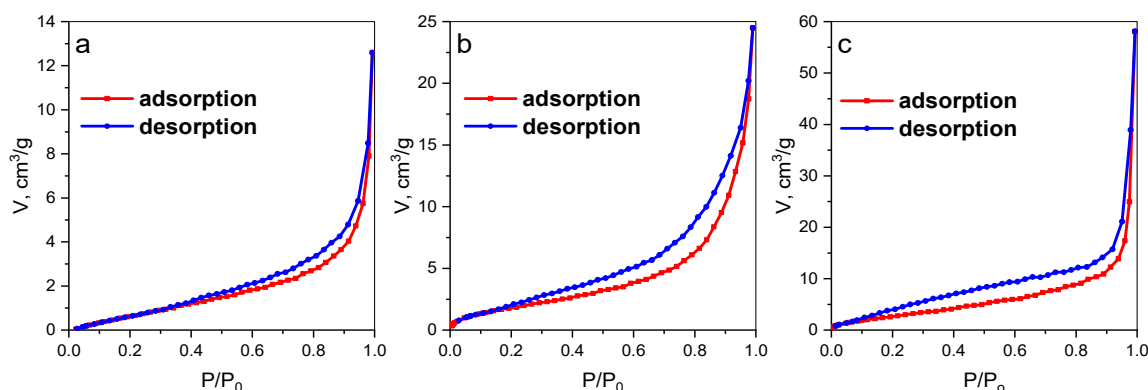


Figure 7. Adsorption-desorption isotherms of nitrogen for (a) HC-200; (b) HC-240; (c) HC-280.

Table 6. Specific surface area and porosity of hydrochars.

Sample	Surface Area, $\text{m}^2\cdot\text{g}^{-1}$	V_s , $\text{cm}^3\cdot\text{g}^{-1}$	V_{mi} , $\text{cm}^3\cdot\text{g}^{-1}$	V_{me} , $\text{cm}^3\cdot\text{g}^{-1}$
HC-200	5	0.0195	0	0.0195
HC-240	8	0.0379	0	0.0379
HC-280	13	0.0899	0	0.0899

V_s = nitrogen adsorption volume; V_{mi} = micropore volume; V_{me} = mesopore volume.

3.6. Thermogravimetric Analysis (TG)

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves presented in Figure 8 describe the SB, HC-200, HC-240, and HC-280 thermal behaviour in the nitrogen atmosphere between 25 and $700\text{ }^{\circ}\text{C}$. According to DTG curves, three distinct and essential stages: dehydration, volatilization, and decomposition have been highlighted [85,86]. The first step usually occurred from room temperature, up to $150\text{ }^{\circ}\text{C}$, and was characteristic for dehydration [40,87,88]. Spruce bark presented a higher mass loss in this step compared with hydrochars (7.48% SB, 1.77% HC-200, 1.55% HC-240, and 1.39% HC-280, respectively). A weak weight loss of moisture in the case of hydrochars were probably due to the hydrochars hydrophobic property. A similar hypothesis was reported for hydrochar obtained from *Miscanthus giganteus*, where the mass loss of water was less than 3% [89].

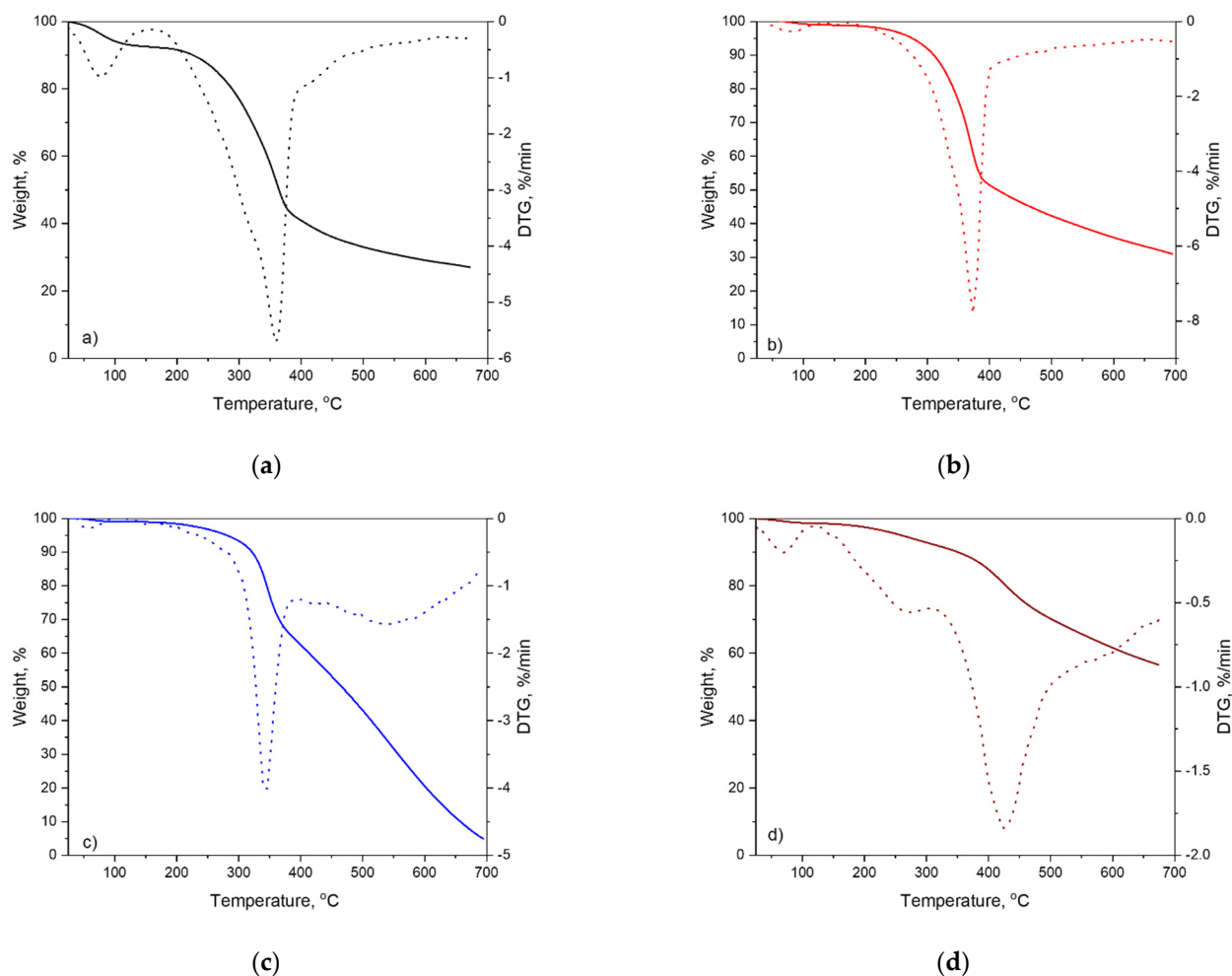


Figure 8. Thermogravimetric (TG) and corresponding derivate thermograms (DTG) for (a) SB, (b) HC-200, (c) HC-240, and (d) HC-280.

For SB, from 200 to 290 °C (with a weak peak at around 267 °C) the decomposition of hemicellulose took place. Cellulose required a higher temperature for decomposition, thus the barely visible peak at 311 °C suggested that cellulose had begun to degrade. The third stage was characteristic for degradation of an aromatic structure with higher molecular weight [87]; in our case, lignin. The most prominent peak at 362 °C confirmed that lignin degradation had started. Similar results for the thermal behaviour of spruce bark (collected from the South of France) were obtained by Diez and co-authors [68], where two lower peak height, at around 300 °C and 350 °C, were corresponding to degradation of hemicellulose and cellulose, and a higher peak near 400 °C was assigned to decomposition of lignin.

The thermal behaviour of HC-200 and HC-240, respectively, were very similar to raw SB. The volatilisation stage took place in the range of 200–350 °C, where the cellulose presented in HC-200 and HC-240 (25.70% and 13.80%, respectively) had suffered a destruction of the long chain, while the decomposition stage characteristic for lignin had occurred at temperatures higher than 350 °C.

For HC-280, some differences in thermal behaviour were identified. The volatilization had occurred in the temperature range of 250–300 °C, with the prominent peak at 275 °C. This was due to the HTC process that already destructed of long chains of hemicellulose and cellulose into short chains compounds. The decomposition stage was predominant and shifted to higher temperatures in the range of 400–500 °C with a prominent peak at 425 °C. Consideration of the main compound in HC-280 was lignin (38.46%), a higher temperature was needed for a complete degradation. With the increase of carbon content

(from 58.26% in SB to 71.61% in HC-280), the HC-280 was more stable and needed a higher temperature for decomposition. Cai and co-authors reported analogous thermal behaviour for hydrochar obtained from tobacco stalk [40].

4. Conclusions

Considering that for a performing HTC process the presence of water is required, the spruce bark waste with 8.35% of moisture content is sustainable to be used as feedstock without preliminary drying.

For the first time, the spruce bark hydrothermal conversion was studied and the main process parameters were assessed. For a good and safe conversion of feedstock during HTC process the recommended parameters are: temperature 280 °C, a residence time for 1 h, and a solid to liquid ratio of 1/5. Hydrothermal conversion was efficient in a single-step low energy consuming process.

The solid product obtained through HTC presented hydrophobic character, a relatively low moisture, and ash content (1.98% and 0.66%, respectively). The FT-IR spectra of feedstock and hydrochars demonstrated the changes in functional groups that allowed for estimations that dehydration, decarboxylation, and aromatization reactions occurred during the HTC conversion of SB.

The elemental analysis showed an increase in C content (71.61%), and a decrease in O and H content (21.11% and 5.20%, respectively). The FT-IR spectra demonstrated that HC-280 presented numerous functional groups, mainly hydroxyls (3500–3000 cm^{−1}), while SEM analysis highlighted the anatomical structure.

These important features led to considering HC-280 as a suitable filler for bio-based composites design. Following this path, the chemical and structural properties of this carbon-rich material will be much better valorized than as solid fuel.

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