Wet and Dry? Influence of hydrothermal carbonization on the pyrolysis of spent grains

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Highlights

- One-step pyrolysis and two-step HTC coupled with pyrolysis was investigated
- Low-temperature HTC in two-step process resulted in similar char yield as pyrolysis
- Coupling of HTC and pyrolysis improved physicochemical properties of pyrochars
- Highest S_{BET} was achieved for hydrochar obtained at 180°C and pyrolyzed at 600 °C

Abstract

Brewer's spent grains (BSG) represent a highly abundant byproduct generated in the beer industry. Owing to abundant availability and high water content, BSG constitutes a raw material of interest for thermochemical conversion *via* hydrothermal carbonization (HTC). Nevertheless, the phyto-toxic effect and low-porosity of hydrochars limit the possible application. Therefore, coupling HTC and pyrolysis may overcome these obstacles. HTC experiments were carried out at 180, 220, and 260 °C and pyrolysis was performed at 400, 600, 800, and 1000 °C to investigate the influence of HTC on the pyrolysis of BSG. Pyrolyzed hydrochars showed lower ash content and higher carbon content compared to char obtained from BSG. The highest surface area (139.5 m² g⁻¹) was obtained for hydrochar produced at 180 °C and then pyrolyzed at 600 °C. This value was 70% higher compared to BSG pyrolyzed at the same temperature (82 m² g⁻¹). The coupling of HTC and pyrolysis showed synergies in the char yield, reduction of ash, increasing of carbon content, and porosity. The promising results proved that at selected process conditions, the novel route is beneficial for carbon materials production due to the improvement of the physicochemical properties of pyrochar at similar mass and carbon yields.

Keywords

biomass; hydrothermal carbonization; hydrothermal pretreatment; pyrolysis; spent grain; two-step process

Nomenclature and abbreviations

HTC- hydrothermal carbonization

S_{BET}- specific surface area calculated using Brunauer-Emmett-Teller model

BSG- Brewer's spent grains

TGA- thermogravimetric analysis

M- moisture content

VM- volatile matter

FC- fixed carbon

HHV- higher heating value

ICP-OES- inductively coupled plasma optical emission spectrometry

TPV- total pore volume

FT-IR- fourier transformed infrared spectroscopy

SEM- scanning electron microscope

TG- mass loss during thermogravimetric analysis

DTG- first derivative of mass loss during thermogravimetric analysis

1. Introduction

Current interest to reduce greenhouse gases attracts attention to the production of biowaste-derived carbon materials. Vast amounts of wet wastes biomasses are available on the market, which are potential feedstocks for biofuels and carbon materials production. Most of the waste streams contain high moisture content, which causes limitation in dry thermochemical conversions due to energy-intensive drying applied before processing, i.e., combustion, pyrolysis, or gasification.

One of the potential feedstock for a thermochemical conversion is Brewer's spent grains (BSG). Beer is ranked in the third-place most consumed beverage in the world, beer production reached an amount of 190 billion liters in 2018 with an approximately 5% of the global market share in Germany (Barth-Haas Group, 2019; Steiner et al., 2015). During the beer production process, different byproducts are formed, one of them being BSG. For example, for 100 liters of brewed beer approximately 20 kg of wet BSG are generated. Germany alone produces about 2 million tons of BSG annually (Mussatto et al., 2006). BSG is rich in sugars, proteins, and minerals, but their chemical composition might differ depending on several factors such as the conditions under it were cultivated, malting and mashing conditions. Independently of all these, BSG are highly rich in fibers (cellulose, hemicellulose, and lignin) and protein, plus a variety of minerals elements, including silicon, phosphorus, and calcium (Mussatto, 2014). Due to the valuable chemical composition, BSG can be used as raw material for the production of important compounds, such as fertilizers, polymers, a component for resins, and activated charcoal (Mussatto, 2014). In this way, biomass upgrading technologies such as hydrothermal carbonization (HTC) and torrefaction have gained renewed interest over the last few years. HTC represents a commonly used sustainable process to convert biomass, as well as their precursors, into carbon materials beneficial for applications including energy storage, electro-catalysis, and

gas storage. HTC was discovered in 1913 when Friedrich Bergius reported the production of synthetic coal from cellulose at high temperatures and pressures under aqueous media (Bergius, 1913). The HTC process and its influence on the solid product have been studied by various researchers, in particular, Kruse et al. (Kruse et al., 2013; Kruse and Dahmen, 2015; Kruse and Zevaco, 2018), Titirici et al. (Titirici et al., 2015, 2012, 2007), Reza et al. (Reza et al., 2016, 2015a, 2014), and Mumme et al. (Mumme et al., 2015, 2011) using different types of feedstocks and a wide range of parameters. The first attempt in performing HTC on BSG has been reported by Heilmann et al. (Heilmann et al., 2011) as an alternative route to drying and combustion, producing hydrochars in relatively mild conditions. Later on, Poerschmann et al. (Poerschmann et al., 2014) and Baskyr et al. (Baskyr et al., 2014), investigated the HTC on BSG reporting a much more detailed study on the chemistry of the process and proposing a way to treat the process water. Ulbrich et al. (Ulbrich et al., 2017) studied the impact of residence time and temperature during HTC, hydrochar properties and CO₂ gasification properties using BSG as feedstock. In this way, they observed that the temperature has more impact on the hydrochar's fuel properties, compared to residence time. Also, the activation energies of the CO₂ reactions are strongly influenced by the temperature, registering a decrease by increasing the HTC reaction severity. Regarding the chemical composition, it is reported that increasing the HTC reaction severity results in an increase in carbon content and a decrease in oxygen content. A pyrolysis study of BSG, has been conducted by Balogun et al. (Balogun et al., 2017). In this way, the authors used a series of characterization techniques, including FT-IR and Raman spectroscopy, corroborated with TGA and XRD data, to describe both the BSG biomass and the resulted biochar, after heat treatment at 500°C, in inert atmosphere. Many outcomes have been underlined, including the potential of the biochar for carbon sequestration and soil amendment applications, and the possibility of extracting fatty acids, such as palmitic, linoleic and oleic acids, that could be

valorized as feedstock for renewable diesel and biodiesel production. Arauzo et al. (Arauzo et al., 2018) used BSG as feedstock for HTC conducting a study with a focus on improving the biomass degradation, control the product distribution, maximize the energy yield and evaluate the effect on chemical compounds in the liquid phase.

In recent studies published by our group (Olszewski et al., 2019a, 2019b), BSG was selected as a potential precursor for a cascade HTC followed by pyrolysis, with a focus on analyzing the pyrolysis behavior of hydrochars produced. HTC applied before pyrolysis decreased the pyrolysis activation energies of hydrochars as well as showed the different composition of volatiles analyzed by PY-GC-MS. Therefore, it brought our attention to analyze the potential of coupling HTC and pyrolysis in a more detailed way.

The aim of this study was to investigate if the two-step process (HTC+pyrolysis) may improve the physicochemical properties of pyrochars compared to one-step pyrolysis. For this purpose, HTC experiments were carried out at three different temperatures i.e. 180 °C, 220 °C, and 260 °C. Afterwards, parent biomass and the obtained hydrochars were pyrolyzed at 400 °C, 600 °C, 800 °C, and 1000 °C. Thermogravimetric analysis and FT-IR spectroscopy of BSG and hydrochars were carried out to verify how the hydrothermal pretreatment changed the structure of original biomass. Mass yield and carbon yield were determined to compare the efficiency of both conversion routes, i.e., pyrolysis, and HTC followed by pyrolysis. Elemental analysis, as well as proximate analysis, was performed to analyze changes caused by HTC applied before pyrolysis. The inorganic content of BSG and hydrochars was measured to check out the removal efficiency of mineral substances during wet conversion. Additionally, N₂ isotherms and SEM micrographs were measured to determine the porosity and surface topography modification generated by the two-step process.

2. Methodology

2.1. Materials

BSG used for experiments were taken from district brewery Hoepfner (Karlsruhe, Germany). The water content of delivered biomass after mechanical dewatering was 75%. The biomass was oven-dried at 105 °C for 24 h to prevent microorganisms activity. Then, dry BSG was stored in plastic zip bags for further experiments.

The HTC was performed in a stainless steel batch reactor of 250 cm³ volume connected to the temperature and pressure sensors for monitoring the process parameters. The reactor was heated up using a modified Gas Chromatography oven (Hewlett Packard, GC 5890), the desired temperature inside of the reactor was reached after approximately 1 hour, with a dwell time of 4 hours. Afterward, the reactor was quenched to the room temperature in the bucket filled with cold water. In a typical experiment, 37.5 g of dry BSG and 112.5 g of deionized water was used to obtain an identical mixture of wet BSG which was delivered from the brewery. The slurry was mixed in the reactor and slightly pressed with a spatula to cover the biomass with water. The hydrochars were produced at 180 °C, 220 °C, and 260 °C under autogenous pressure. The experiments were made in 4-5 replicates to obtain enough material for further pyrolysis, followed by mixing and grinding in order to obtain a homogeneous powder for further investigations. The samples were labeled as follow HTC-X, where X is the temperature of the HTC process.

Raw biomass and three hydrochars (HTC-180, HTC-220, and HTC-260), produced as described above, were pyrolyzed in muffle oven in oxygen-free atmosphere provided by the constant flow of nitrogen gas (5 L min⁻¹). The pyrolysis experiments were carried out for all materials at 400, 600, 800, and 1000 °C. Approximately 3 g of each material (powder) was evenly placed into alumina crucible (VWR, Germany) covered with lid (VWR, diam. 45 mm) and placed into the preheated oven, with a residence time of 2 h. After the reaction time, the

samples were taken out from the muffle oven and allowed to cool down to room temperature under N₂ flow. The experiments were repeated 4-10 times to obtain ca. 5 g of each pyrochar for further analysis. Then the pyrochars were mixed and ground to reduce particle size below 200 µm, and stored in glass containers. The samples were labeled as Py-Y-BSG for biomass and Py-Y-HTC-X for hydrochars. Y and X corresponded to the temperatures of pyrolysis and HTC process, respectively. For example, Py-600-HTC-220 is hydrochar produced at 220 °C then pyrolyzed at 600 °C.

The mass yield of hydrochars and pyrochars is defined in Eq. 1.

$$Y_M = m_p / m_s \quad (1)$$

Where, Y_M, m_p, and m_s correspond to char mass yield (wt.%), the mass of the obtained solid product (g, dry basis), and the mass of the used substrate (g, dry basis), respectively.

The formula for the calculation of carbon yield to char is expressed in Eq. 2.

$$Y_C = Y_M \cdot C_p / C_b \quad (2)$$

Where, Y_C, C_p, C_b are carbon yield to char (wt.%), the carbon content in char (wt.%, dry basis), and carbon content in biomass (wt.%, dry basis).

2.2. Thermogravimetric, proximate, and elemental analysis

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 F5 Jupiter analyzer (Germany). The measurements were conducted in an inert atmosphere, using N₂ with a flow rate of 100 cm³ min⁻¹. The samples were placed in alumina crucibles and measured as follows: i) heated from 40 °C to 105 °C with a heating rate of 20 °C min⁻¹, ii) held 10 min in isothermal conditions, at 105 °C, to remove the moisture, and iii) heated up to 800 °C with a

heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. For each measurement (TGA and proximate analysis), approximately 20 mg of material was used.

Proximate analysis using TGA was carried out according to PerkinElmer guideline 'Proximate Analysis of Coal and Coke using the STA 8000 Simultaneous Thermal Analyzer' (Cassel et al., n.d.) adjusted to the Netzsch analyzer. The temperature program during the measurement was as follow: i) heated up from 40 to $105\text{ }^{\circ}\text{C}$ with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$; ii) held 10 min in isothermal conditions to determine a moisture (M) content; iii) heated up to $950\text{ }^{\circ}\text{C}$ with a heating rate of $40\text{ }^{\circ}\text{C min}^{-1}$; iv) held 10 min in isothermal conditions to determine a volatile matter (VM) content; v) held 30 min in isothermal condition in oxidizing atmosphere to determine ash content. Steps (i-iv) were carried out in an inert atmosphere using N_2 flow rate of $100\text{ cm}^3\text{ min}^{-1}$, for the last step (v) the carrier gas was changed to synthetic air, using the same flow, to burn the carbonized sample. The measurements were made in duplicates; the average data are reported. The M, VM, and ash were determined based on local minimum value on the thermogravimetric curve in steps ii), iv), and v), respectively. The difference between the sum of measured ash and VM contents (dry basis) from 100% is the value of fixed carbon (FC) (Ahmad et al., 2017).

Elemental analysis of all investigated materials was measured according to the DIN-51732 standard. The measurements were carried out using EuroEA3000 CHNS Analyzer (HEKAtech GmbH, Germany). The oxygen content was calculated by subtracting the sum of measured elements (C, H, N, S) and ash expressed on a dry basis from 100%. Each sample was analyzed twice; the average data are reported.

Channiwala and Parikh equation (Eq. 3) was used to calculate the higher heating value (HHV), (MJ kg^{-1}) (Channiwala and Parikh, 2002). The formula is characterized by high accuracy, and it is presented as follow:

$$HHV = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034O - 0.0151 \cdot N - 0.021 \cdot A \quad (3)$$

Where C, H, S, O, N and A represents carbon, hydrogen, sulphur, oxygen, nitrogen, and ash content of analyzed material (wt.% dry basis), respectively.

2.3. ICP OES

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the content of inorganic elements contained in BSG and derived hydrochars. The measurements were carried out using a 715 Series ICP-OES apparatus (Agilent Technologies, USA). About 0.2 g of each material was digested in the mixture of 10 mL 65 wt.% Suprapur® HNO₃ (Merck KGaA, Germany) and 1 mL 30 wt.% Suprapur® HCl (Merck KGaA, Germany) using a Discover microwave digester (CEM, Germany). MilliQ water was added to the digested mixtures to obtain a 25 mL of solution. The samples were diluted 10 times, with 1 wt.% HNO₃, before the measurements.

The elements distribution (mg of element/g of biomass) in hydrochars was calculated using the following formula:

$$E_D = Y_M \cdot W_H \quad (4)$$

Where Y_M and W_H corresponded to mass yield of hydrochar and the mass fraction of detected element in this hydrochar (mg g⁻¹), respectively. For BSG E_D=W_{BSG}.

The removal factor (%) was calculated to estimate the efficiency of washing inorganic elements (Ca, Fe, K, Mg, Mn, Na, P, Zn) out of hydrochars during HTC.

$$R = \frac{W_{BSG} - E_D}{W_{BSG}} \cdot 100\% \quad (5)$$

Where W_{BSG} and E_D represented a mass fraction of detected elements in BSG and elements distribution in the hydrochar, respectively.

2.4. Surface area

The N₂ adsorption isotherms were measured to determine the surface area of pyrolyzed materials using a Nova 4000e analyzer (Quantachrome Instruments, USA). The analysis was carried out at N₂ boiling point (-196 °C) according to the ISO 9277:2010 standard. Before the adsorption measurements, the samples were degassed at 180 °C for at least 20 hours. Brunauer-Emmett-Teller (BET) model was used to calculate the specific surface area (S_{BET}). The total pore volume (TPV) was calculated using the Density Functional Theory.

2.5. FT-IR

Fourier transformed infrared spectroscopy graphs were obtained using a Tensor 27 FTIR spectrometer equipped with attenuated total reflector (ATR) (Bruker, USA). All samples were scanned between 4000-400 cm⁻¹ and using 32 scans min⁻¹, in transmittance mode. Around 10 mg of dry material was used for each measurement. The sample was spread on the diamond surface and pressed with a metal rod. All measurements were carried out at room temperature.

2.6. SEM

Micrograph images were obtained with a Scanning Electron Microscope (SEM) FEI Quanta 3D (Thermo Fisher Scientific, USA). The sample distance from the objective lens was 18 mm. The electron source operated at an excitation voltage of 10 kV. The samples were distributed on a conductive pad and put in the measuring chamber. The samples were covered with Au to avoid charging during the observation.

3. Results

3.1. Process yield

The mass yields of the one-step (i.e., direct pyrolysis) and the two-step (i.e., HTC followed by pyrolysis) process are presented in Fig. 1A. The first left bar in Fig. 1A is equal to 100% and are shown as a reference. HTC of BSG was analyzed firstly, hydrochars showed a notable reduction of mass relative to the original material. It was observed that at lower temperatures of the process resulted in a higher mass yield of the hydrochar, achieving maximum hydrochar yield (69.8 wt.%) at 180 °C. The consistent increase in the temperature resulted in a yield of 49.5 wt.% at 220 °C. Consequently, the lowest hydrochar yield, i.e., 38.4 wt.%, was obtained at 260 °C. As the next step, biomass and produced hydrochars were pyrolyzed to compare the one-step pyrolysis process with the two-step process. Pyrolysis showed a similar trend like HTC, but the process was less temperature sensitive due to a much higher temperature range (400-1000 °C) compared to HTC (180-260 °C). The char yields of one-step pyrolysis of initial BSG were 33.0, 25.5, 23.1, and 20.0 wt.% at 400, 600, 800, and 1000 °C, respectively. Moving to the pyrolysis of hydrochars (scatters in Fig. 1A), it can be observed that the char yields are higher than char directly from biomass at each pyrolysis temperature. Besides, a trend is visible while increasing the temperature of HTC resulted in a higher char yield for pyrolyzed hydrochars. However, the initial loss that occurred during the HTC must be taken into account, to reliably compare the overall char yield of the two-step to the one-step pyrolysis of BSG. The overall mass yield to char is presented as bars in Fig. 1A. The averaged results showed that BSG after low-temperature (180°C) HTC had a similar or even higher overall char yield in comparison to direct pyrolysis of BSG. Such a small difference is in the error range of the measurements. Higher temperatures during HTC resulted in lower overall conversion to char. The most significant discrepancies in conversion within analyzed materials occurred at the lowest pyrolysis temperature, i.e., 400 °C.

The final char yields at this temperature were 33.1, 33.5, 25.4, and 23.4 wt.% for Py-400-BSG, Py-400-HTC-180, Py-400-HTC-220, and Py-400-HTC-260, respectively. Further increase in temperature during the pyrolysis process resulted in a relative reduction of these differences. The experiments carried out at 1000 °C have shown the lowest char yield, i.e., 20.0, 21.4, 18.2, and 17.2 wt.% for Py-1000-BSG, Py-1000-HTC-180, Py-1000-HTC-220, and Py-1000-HTC-260, respectively.

Every step of conversion applied to treat biomass results in the distribution of carbon to different products created during the process. This study emphasizes the properties of solid residue from both processes, i.e., char. Other products (liquid and gas) generated during HTC and pyrolysis are not characterized herein. Fig. 1B shows the carbon yield to final char calculated according to Eq. 2. The values illustrate the amount of carbon transformed from the feedstock into final char – the first left bar in Fig. 1B (BSG in section HTC) corresponds to initial carbon contained in the biomass. The results of the carbon yield to char partly reflect the mass yield. Fig. 1B showed that the mildest HTC treatment condition (180 °C) of BSG had the highest carbon yield to char. An increment of the HTC temperature resulted in the loss of carbon, which remained in the char (i.e., the carbon content was higher, but the mass yield of char was reduced). Pyrolysis of biomass and derived hydrochars showed the same trend.

Fig. 1. Comparison of mass and carbon yields for one- and a two-step process. A- shows the mass yields to char. Scatters represent pyrolysis char yield for hydrochars. Bars represent HTC and pyrolysis yield for BSG, and overall mass yield after the two-step process for hydrochars. B- shows the carbon yield to char.

3.2. Materials characteristic

The physicochemical properties of BSG, hydrochars, and pyrochars are presented in Table 1. BSG was characterized by a high content of VM (78.4 wt.%) and relatively low ash content (4.77 wt.%). The carbon content of the dry BSG was around 50 wt.%, and the nitrogen content was around 5% due to the high amount of protein (McCarthy et al., 2013; Niemi et al., 2012). These values are similar to the BSG analysis published by Balogun et al. (Balogun et al., 2017); they reported slightly lower nitrogen content (3.5 wt.%).

HTC of BSG resulted in the reduction of VM content in the hydrochars due to the conversion of biopolymers contained in the biomass structure (mainly hemicellulose, cellulose, lignin, and proteins) (Fan et al., 2018; Peterson et al., 2010; Titirici et al., 2012). The VM content for hydrochars was in the range of 54.6-70.5 wt.%, while higher temperatures during the HTC resulted in a lower value, due to more conversion. Consequently, the FC value rose up from 16.8 wt.% for BSG up to 38.6 wt.% for HTC-260. The ash content after HTC was in the range of 4.2-6.8 wt.%. The values remained at a similar level as the feedstock, despite weight loss during the

conversion. The loss indicates that some mineral components were washed into the liquid reaction medium. The inorganic elements contained in BSG and derived hydrochars determined by ICP-OES are shown in Fig. 2A while Fig. 2B presents the removal efficiency of individual elements during HTC. The main detected elements were P, Ca, Mg, and K, respectively. Zn, Fe, Mn, and Na were also found in trace amounts. The highest removal efficiency (about 50% or more) was achieved for K, Na, Mg, and P. Additionally, HTC increased the carbon content (60.6-69.5 wt.%) and reduced oxygen content (12.4-23.7 wt.%) of produced hydrochars. Besides, the nitrogen values remained unchanged, and the hydrogen content slightly decreased.

Fig. 2. Composition of inorganic elements measured by ICP-OES. A-shows elements distribution expressed based on input BSG, B-shows removal efficiency during HTC.

Pyrolysis resulted in a much higher reduction of volatiles compared to HTC, for both BSG and hydrochars. The VM content was in the range of 22.9-30.8 wt.% for pyrolysis at 400 °C and 9.0-13.3 wt.% at 600 °C. Higher pyrolysis temperatures resulted in the VM content of 5.6-9.3 wt.% at 800 °C and 2.7-4.7 at 1000 °C. In general, the more severe conditions during the HTC resulted in a lower content of volatiles at the same pyrolysis temperature. The ash showed a different behavior during pyrolysis compared to HTC, being in the range of 7.6-10.3 wt.% for

400 °C, and increasing with increasing the pyrolysis temperature up to 1000 °C (8.5-14.4 wt.%). Within the same pyrolysis temperature, the ash content was the highest for BSG and the lowest for HTC-180. The carbon content of the pyrochars obtained in low-temperature pyrolysis (400 °C) was in the range of 66.8-70.5 wt.%. Pyrolysis of BSG at 400 °C showed lower carbon content than hydrochar produced at 260 °C. Further raising the temperature during pyrolysis caused an increase in the carbon content in the pyrochars due to higher carbonization degree (Mochidzuki et al., 2003). Pyrochars had a carbon content in the range of 72.0-79.9, 73.6-79.3, and 78.7-83.5 wt.% at 600, 800, and 1000 °C, respectively. The results showed a trend that the lowest carbon content in the pyrochars was found for BSG and the highest for HTC-220. HTC-180 and HTC-260 were characterized by similar carbon content. The increase in carbon content during pyrolysis is balanced by a considerable drop in oxygen and hydrogen content. Besides, all the hydrochars showed similar nitrogen values within the same pyrolysis temperature. The nitrogen content in pyrochars produced from BSG was slightly higher compared to pyrolyzed hydrochars. In both cases, the higher temperature of dry conversion caused a drop in the nitrogen content which took values of 3.9-7.1 wt.% for Py-BSG and 3.9-5.9 wt.% for Py-HTC.

The estimated HHV for BSG was 20.69 MJ kg⁻¹ (dry basis). HTC caused an increase in the HHV and the HHV for hydrochars was in the range of 24.69 MJ kg⁻¹-28.37 MJ kg⁻¹. In general, the highest HHV was obtained for HTC-260. The HHV values determined for pyrochars were lower than those obtained for hydrochars.

The BET surface area for pyrochars is shown in Table 1. N₂ adsorption-desorption isotherms revealed moderate porosity both for pyrolyzed BSG and for pyrolyzed hydrochars. The BET surface area varied between 5 m² g⁻¹ and 139.5 m² g⁻¹. As a general trend, it can be observed that by increasing temperature from 400°C to 600°C, the surface area register an abrupt increment, being more than 10 times larger. Pyrochars produced at 600 °C revealed substantial

surface areas and their N₂ isotherms are presented in Fig. A1 (Appendix A). The adsorption-desorption isotherms, according to the IUPAC classification, showed type IV adsorption isotherms, with characteristic hysteresis, which corresponded to mesoporous material (Allothman, 2012). The surface area for Py-600-BSG achieved 82 m² g⁻¹. The highest S_{BET} (139.5 m² g⁻¹) was reached for Py-600-HTC-180, the higher temperatures during HTC resulted in lower surface area, i.e., 94.9 m² g⁻¹ for Py-600-HTC-220 and 68.5 m² g⁻¹ for Py-600-HTC-260. Pyrolysis at 800 °C and 1000 °C contributed to a massive reduction of the surface area of investigated materials. The two-step process was no longer favored due to lower surface areas of pyro hydrochars compared to the one-step pyrolysis of BSG. The total pore volume (TPV) strongly depends on the surface area, therefore the highest value was achieved for Py-600-HTC-180

In the case of hydrochars, the adsorption was not measured due to technical problems. We observed that some oil was condensed on the measuring cells despite the low temperature (180 °C) during the degassing of the BSG and hydrochars samples. For this reason, we decided to skip these measurements.

1 *Table 1*
2 *Physicochemical properties of BSG and derived chars.*

Sample	Proximate analysis, wt.%, db				Elemental analysis, wt.%, db					HHV, db	Texture	
	Moisture	VM	Ash	FC	C	H	N	S	O	(MJ kg ⁻¹)	SBET (m ² g ⁻¹)	TPV [cm ³ g ⁻¹]
BSG	4.25	78.40	4.77	16.83	50.17	7.07	5.22	0.14	32.63	20.69	n.m.	n.m.
HTC-180	0.88	70.51	4.22	25.27	60.59	6.43	4.87	0.24	23.65	24.69	n.m.	n.m.
HTC-220	0.62	64.04	4.86	31.10	65.90	6.48	5.13	0.09	17.54	27.04	n.m.	n.m.
HTC-260	0.44	54.63	6.75	38.62	69.52	6.40	4.95	0.04	12.34	28.37	n.m.	n.m.
Py-400-BSG	2.29	28.62	10.27	61.12	66.84	3.65	7.08	n.d.	12.16	23.15	5.0	0.007
Py-400-HTC-180	1.85	30.76	7.56	61.68	69.22	3.95	5.87	0.13	13.27	24.99	7.2	0.010
Py-400-HTC-220	2.05	22.86	9.35	67.79	70.50	3.52	5.86	0.14	10.63	24.83	5.9	0.011
Py-400-HTC-260	1.20	25.43	9.59	64.99	70.47	4.09	5.62	0.14	10.09	25.53	3.4	0.008
Py-600-BSG	3.69	13.32	11.97	74.71	72.49	1.77	6.66	0.05	7.06	23.15	82.0	0.058
Py-600-HTC-180	3.26	12.13	9.20	78.67	75.58	1.96	5.82	0.08	7.36	25.13	139.5	0.098
Py-600-HTC-220	3.14	10.33	9.32	80.34	76.48	1.99	5.87	0.09	6.25	25.56	94.9	0.071
Py-600-HTC-260	2.37	8.96	11.26	79.78	75.30	1.78	5.75	0.09	5.82	24.56	68.5	0.056
Py-800-BSG	5.27	9.32	11.56	79.12	73.62	0.74	6.16	0.06	7.86	22.41	27.6	0.025
Py-800-HTC-180	5.62	7.44	7.52	85.04	78.60	1.03	5.24	0.10	7.51	25.52	24.1	0.024
Py-800-HTC-220	5.22	6.25	7.49	86.26	79.26	0.80	5.38	0.12	6.95	25.52	9.9	0.007
Py-800-HTC-260	4.31	5.57	10.28	84.15	78.01	0.76	5.47	0.12	5.36	24.60	4.9	0.004
Py-1000-BSG	3.25	4.24	14.42	81.34	78.72	0.31	3.89	0.07	2.59	23.97	17.2	0.019
Py-1000-HTC-180	4.10	4.70	8.52	86.78	81.77	0.37	3.99	0.10	5.25	26.06	10.8	0.013
Py-1000-HTC-220	1.63	3.89	9.80	86.31	83.45	0.28	3.93	0.15	2.39	26.58	8.1	0.008
Py-1000-HTC-260	1.83	2.65	12.25	85.10	81.47	0.25	4.23	n.d.	1.80	25.34	6.4	0.006

db – dry basis

n.d. – not detected

n.m. – not measured

3.3. TGA

The thermal decomposition of BSG and derived hydrochars was investigated using the thermogravimetric analyzer. Fig. 3A shows mass loss (TG) and Fig. 3B presents the first derivative of mass loss (DTG) as the functions of temperature. The decomposition of BSG showed the lowest thermal stability due to the smallest char residue after TGA. HTC of BSG increased the thermal stability of hydrochars; the highest thermal stability was achieved for HTC-260. DTGs curves showed that all materials started to decompose around 150 °C. DTG curve for BSG had a typical pattern for lignocellulosic biomass decomposition where characteristic peaks for degradation of structural biopolymers (hemicellulose, cellulose, and lignin) are visible (Yang et al., 2007). The most in-depth peak (DTG₁) for BSG was located at 283 °C. The next peak (DTG₂) occurred at about 350 °C, and the remaining peak (DTG₃) was found at 420 °C. HTC caused a change in the shape of DTG curves for hydrochars. The first peak for hydrochars (DTG₁*) was largely reduced and moved to a lower temperature (250 °C) compared to DTG₁. The highest intensity of the DTG₁* was achieved for HTC-220 and the lowest equally for HTC-180 and HTC-260. The peak DTG₂ was located at this same temperature both for BSG and derived hydrochars. Hydrochar produced at 180 °C had a similar height of the peak DTG₂ compared to BSG. Further increase of HTC temperature (i.e., HTC-220) caused a reduction of DTG₂ peak intensity. Eventually, DTG₂ peak was not presented anymore for HTC-260. On the other hand, peak DTG₃ became clearly visible and increased its intensity for hydrochars. The highest value of peak DTG₃ was obtained for HTC-260 while the lowest value was reached for HTC-180.

Fig. 3. Thermogravimetric analysis of BSG and derived hydrochars. A-shows mass loss (TG) as a function of temperature, B-shows the first derivative of the mass loss (DTG) as a function of temperature.

3.4. FT-IR

The biomass and hydrochars were analyzed by FTIR spectroscopy (Fig. 4A). The hydrochars presented the typical structure for the hydrothermal carbon (Nizamuddin et al., 2019; Titirici et al., 2007). In this way, the broadband in the region $3600\text{--}3300\text{ cm}^{-1}$ was attributed to the O-H groups (e.g., water, alcohol, and phenol). This band was also present in the raw biomass spectra, and it can be observed that by increasing the HTC temperature, the intensity of the O-H groups is decreasing, mainly due to deoxygenation and dehydration during HTC (Fangyu et al., 2019). This is in agreement with EA results (Table 1), which showed a decrease in the oxygen content by enhancing the HTC temperature. Moreover, the decrease in hydroxyl and carboxyl contents can increase the hydrophobicity of the hydrochar (Kambo and Dutta, 2014). C-H aliphatic (CH_3 - and CH_2 -) and aromatic stretching vibrations can be identified between 3000 and 2800 cm^{-1} (Gao et al., 2016), both for hydrochars and for the BSG. The band around $\sim 1700\text{ cm}^{-1}$ corresponds to C=O present in ketones, aldehydes, quinone, esters, and carboxylic acid functional groups. Transmittance intensity weakened with the increase in HTC temperature because of decarboxylation and dehydration reactions during HTC (Fangyu et al., 2019). The band at ~ 1600 -

1630 cm^{-1} , could be attributed to primary amides, while the one at $\sim 1500 \text{ cm}^{-1}$ can be assigned to the C-N stretching and N-H in-plane bending absorption due to the secondary amides from proteins. By performing HTC at a higher temperature, those bands were decreasing in intensity, as an indication of the decomposition of nitrogen functional groups, and the formation of volatile compounds. It was also observed in EA data (Table 1) that the nitrogen content decreased with increasing HTC temperature. The band at $\sim 1400 \text{ cm}^{-1}$ corresponds to aromatic C, indicative of lignin like structure and the bands between 1200 cm^{-1} and 1110 cm^{-1} are associated with the stretching of C-O bonds (carboxyl, ester, and ether groups) and OH deformations of carboxylic groups (Gao et al., 2016). The intensity of C=C and C-O stretching vibrations was weakened with the increase in the HTC temperature as an indication of partial decomposition of lignin (Kambo and Dutta, 2014). FTIR spectra have been recorded for the pyrolyzed samples (Fig. 4. B-C and Fig. A2.), as well. When compared on horizontal, it is visible that by increasing the pyrolysis temperature, the band in the region $3600\text{-}3300 \text{ cm}^{-1}$ disappears, as well as the aliphatic functional groups, as an indication of surface oxidation. Also, the other bands ($1750\text{-}500 \text{ cm}^{-1}$) decreased in intensity, as more volatile compounds were formed. Having a look at the samples pyrolyzed at the same temperature, but a variation on the HTC step (Fig. 4. B-C and Fig. A2.), it can be observed that they present similar structures, and this is due to the pyrolysis step, which was the same for all of them. However, it can be noticed that the HTC step has a visible effect, by adding more functional groups according to the peak at $\sim 1700 \text{ cm}^{-1}$ corresponding to C=O, which is absent in BSG-400, and weak in BSG-600, but present in BSG, Py-400-HTC-180 and Py-600-HTC-180, as well as for the 220°C hydrochars.

Fig. 4. FTIR spectra for A the hydrochars, B pyrolyzed samples at 400°C, and C pyrolyzed samples at 600°C.

3.5. SEM

SEM micrographs of the pyrolyzed BSG are displayed in Figure 5. The results show the formation of heterogeneous systems with irregular particle shapes. The pyrolysis step provoked the release of organic matter due to the decomposition of biomass. The thermochemical conversion promoted shrinkage, melting, and cracking of the structure which resulted in an improvement of porosity (Batista et al., 2018). That fact can be corroborated with the BET surface areas displayed in Table 1, the surface area is highly improved from $5 \text{ m}^2 \text{ g}^{-1}$, in case of BSG-PY-400, to $82 \text{ m}^2 \text{ g}^{-1}$, for BSG-PY-600. After this, the surface area starts to decrease, which might be an indication of pore collapse and aromatization of the char. According to proximate analysis data, the ash content increases by increasing the pyrolysis temperature, being more or less constant in between 600°C and 800°C , and reaching a maximum at 1000°C of about 14%. Moreover, enhancing the conditions of the heat treatment results in the formation of more volatile compounds (Zhao et al., 2017), which can be the reason of the morphology changing. SEM measurements were carried out for the pyrolyzed hydrochars, as well. Having a look at the one-step synthesis material (e.g., Py-600-BSG, Fig. 6A) and the two steps approach (i.e., Py-600-HTC-180-260, Fig. 6B-D) it can be observed that HTC step does not have any significant impact on the morphology of the material. The samples prepared *via* HTC and pyrolysis displayed heterogeneous structures with nonuniform particle shape.

Fig. 5. SEM micrographs of the BSG pyrolyzed at different temperatures A. 400°C, B. 600°C, C. 800°C, and D. 1000°C.

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93 *Fig. 6. SEM micrographs for A. pyrolyzed biomass at 600°C, and B-D pyrolyzed hydrochars (prepared via HTC of BSG at different temperatures) at the same temperature.*

4. Discussion

4.1. Effect of HTC on the yield of the final product

HTC of BSG resulted in the reduction of VM content and the increase in carbon content in the hydrochars due to the conversion of biopolymers that form the biomass structure mainly hemicellulose, cellulose, lignin and proteins (Fan et al., 2018; Peterson et al., 2010; Titirici et al., 2012). Funke et al. (Funke and Ziegler, 2010) reported that many different reaction mechanisms occurred during HTC, i.e., hydrolysis, dehydration, decarboxylation condensation, aromatization, and polymerization. The less stable biopolymer contained in the biomass is hemicellulose, which undergoes hydrolysis at about 180 °C in subcritical water condition. Cellulose is the next structure, which is degraded during HTC. The less stable parts of amorphous cellulose starts to hydrolyze above 200 °C (Peterson et al., 2008). DTG curves (Fig. 3B) obtained in this study reflected these phenomena very well. TGA of BSG showed peak DTG₁, which corresponded to the decomposition range of hemicellulose (250-330 °C) (Li et al., 2018; Reza et al., 2014). However, after HTC peak DTG₁ was removed for all hydrochars which confirmed that the hemicellulose was converted even at 180 °C due to the lack of strong glycosidic bonds and random structure of the biopolymer (Peterson et al., 2008). Peak DTG₂ is related to the degradation of cellulose and usually breaks down at 350-420 °C (Shen et al., 2015). However, BSG contains a high amount of protein, which decomposes at 200-500 °C, which may overlap with the degradation of hemicellulose and cellulose (Ricci et al., 2018). Herein, the height of peak DTG₂ for BSG and HTC-180 was at the same level, which showed that cellulose stayed unreacted in mild HTC conditions (180°C). Further increase in HTC temperature resulted in a substantial reduction of the peak DTG₂ for HTC-220. However, the 4 h reaction time was not enough to fully convert the cellulose contained in BSG at 220 °C due to the relatively slow kinetics of hydrolysis caused by the presence of very stable hydrogen bonds and higher

cristalinity in the structure of cellulose (Peterson et al., 2008). This result is consistent with our previous study (Olszewski et al., 2019a). HTC at 260 °C resulted in the disappearance of the peak DTG₂ which verified a full conversion of cellulose. Besides HTC resulted in the creation of different structures reflected by peaks DTG_{1*} and DTG₃ (Fig. 3B), which showed how the parent biomass is transformed during the process. These peaks are related to the decomposition of intermediate carbonization products, i.e., aromatic products created in Maillard-type reactions and newly created structure of hydrochars (Kruse and Zevaco, 2018; Olszewski et al., 2019a).

HTC of BSG has been investigated by a few researchers, including Poerschmann et al. (Poerschmann et al., 2014), Ulbrich et al. (Ulbrich et al., 2017), Velebil et al. (Velebil et al., 2016), and Arauzo et al. (Arauzo et al., 2018). The more detailed comparison within the yields and properties of hydrochars produced from BSG was described in the previous study (Olszewski et al., 2019b). In general, the hydrochar yield is inversely proportional to the temperature of the HTC. Increasing the temperature of the HTC process has a much more significant effect on conversion than extending the reaction time. The hydrochar yield produced from BSG is in the range of ~38 wt.% at higher temperatures (HTC-260 reported in this study) and can reach the yield up to ~73 wt.% at 180 °C (Velebil et al., 2016). The results obtained in this study are consistent with the subject literature. The small discrepancies between the results arise from the different origin of the feedstock, another ratio of water to dry matter, as well as different reactor configuration and related differences in the heat transfer.

4.2. Novel two-step cascaded HTC and pyrolysis process

Our previous study (Olszewski et al., 2019a) focused on pyrolysis kinetics of hydrochars showed that HTC prior pyrolysis of BSG reduced the pyrolysis activation energies. Similar results using sewage sludge were obtained by Ma et al. (Ma et al., 2019). It can be stated that hydrochars revealed different behavior during pyrolysis than parent biomass. HTC converted the biomass differently than pyrolysis while the reaction takes place in the subcritical water. Due to the presence of a liquid reaction medium, the bio-components firstly undergo hydrolysis and then in consequents reactions create a new structure of the material (Fig. 3B). On the other hand, pyrolysis resulted in devolatilization of less stable parts of the biomass. During pyrolysis of BSG hemicellulose is decomposed at very beginning resulting in huge mass reduction. Consequently, much carbon is irretrievably lost in the form of VM, which is confirmed by proximate analysis (Table 1). Hydrochars resulted in much higher VM content compared to pyrolysis of BSG at 400 °C.

The nitrogen behavior during the processing of BSG was notable. In general, proteins are not thermally stable and start to break down at mild pyrolysis conditions. Ricci et al. (Ricci et al., 2018) researched the thermal degradation of isolated proteins from different legumes (lentils, peas, and beans). They reported that proteins degraded in the temperature range of 200-500 °C with a peak at 330 °C. Our previous study showed that low-temperature pyrolysis (300 °C) of BSG resulted in the release of more amounts of N-compounds during PY-GC-MS analysis compared to hydrochars (Olszewski et al., 2019b). Herein, the pyrolyzed hydrochars resulted in lower nitrogen content than pyrolyzed BSG (Table 1) due to the conversion of nitrogen compounds during HTC. The proteins contained into BSG were hydrolyzed to amino acids in subcritical water during HTC (Arauzo et al., 2018; Kruse et al., 2016). In consecutive reactions, amino acids were transformed into ammonia and amines. Subsequently, part of ammonia and

amino acids were dissolved in the reaction medium leading to the lower nitrogen content in hydrochars compared to BSG. In the case of BSG, due to the high content of carbohydrates and proteins, the critical role was played by Maillard-type reactions in which hydrolyzed amino acids reacted with reducing sugars (Fan et al., 2018; Peterson et al., 2010; Titirici et al., 2012) resulting in the formation of N-containing heterocyclic compounds integrated into the structure of the hydrochars (Falco et al., 2012; Kruse et al., 2016).

The next important aspect is the ash content in the pyrochars. The part of ash was removed during HTC, and due to the mass reduction in the process, pyrolyzed hydrochars resulted in lower ash content than pyrolyzed BSG (Table 1). The removal of inorganics is caused by dissolving K, Na, and Mg salts (phosphates, carbonates, and chlorides) in subcritical water (Heilmann et al., 2014; Huang et al., 2017; Kruse and Dahmen, 2015) which is also confirmed by ICP-OES results (Fig. 2). The decrement of ash content in pyrolyzed hydrochars may result in a decrease in transportation costs as well as bring benefit for further applications, for example, as a precursor for activated carbon production.

Attention should be paid to the pyrolysis of hydrochar produced at 180 °C. The results indicated that the pyrolysis of HTC-180 has been beneficial due to the higher yield of carbon to the char compared to one-step pyrolysis of plain BSG (Fig 1 B). The coupling of both thermochemical processes reduced the losses of carbon into volatiles during pyrolysis, so more carbon supplied in biomass was converted to the char. Low-temperature HTC brought a benefit for a cascade type process due to a relatively small mass reduction in the process and at the same time removing some inorganic compounds as well as changing the structure of initial biomass. Pyrolysis of hydrochars resulted in modification of texture properties of pyrochars (Table 1). Py-600-HTC-180 showed 70% higher surface area ($139.5 \text{ m}^2 \text{ g}^{-1}$) compared to Py-600-BSG ($82.0 \text{ m}^2 \text{ g}^{-1}$), which was obtained in one step process. These values for the surface area were relatively

low, which is confirmed by SEM images (Fig. 6), which show unorganized and highly unporous structures of the investigated materials.

We suspect that the increased porosity for pyrolyzed hydrochar is caused by the conversion of hemicellulose during HTC, which is partly converted into a more stable structure, meanwhile cellulose stayed unchanged. This is important, because cellulose is mainly responsible for structure and porosity development during pyrolysis and activation (Cagnon et al., 2009; Contescu et al., 2018). The highest surface area at 600 °C may be related to the fact that increasing the temperature during pyrolysis released more VM, which can help to improve porosity by expanding the structure and create defects. Above 600 °C, the rate of mass loss is reduced, and the TGA and DTG curves flattened (Fig. 3). At high temperatures, mainly reorganization and aromatization of the structure occurs, which enhance the electrochemical properties of the chars (Mochidzuki et al., 2003). On the other hand, higher pyrolysis temperature (above 700 °C) led to a decrease in the surface area as well as pore volume (Table 1) due to pore widening, shrinkage, and collapse (Fu et al., 2011; Mochidzuki et al., 2003).

This study showed that increasing the HTC temperature to 220 °C in the two-step process is no longer beneficial due to the reduction of the carbon conversion as well as a decrease in the final pyrochar yield (Fig. 1A). Despite the fact that the carbon content and surface area of the pyrochar were slightly higher compared to one-step pyrolysis of BSG. On the other hand, higher temperatures of HTC may be favorable when looking at one-step HTC and its broad application in advanced carbon material production such as magnetic hydrochars (Reza et al., 2015b), N-doped hydrochars (Titirici et al., 2012), hydrochar-zeolite composite (Mumme et al., 2015), as well as metal dopped (Ni, Ru) hydrochars (Ding et al., 2012; Hoffmann et al., 2019).

Tailor-made carbon materials can be synthesized using HTC as a pretreatment step due to different reaction mechanisms occurring in the sub-critical water environment than dry

conversion methods. It is possible to design and predict which components (hemicellulose, cellulose, and lignin) and to which extent should be converted during HTC to optimize the properties of final chars. By coupling HTC with another post-treatment process, such as pyrolysis or activation, should be considered that higher temperatures of HTC favorize the loss in material yield as well as carbon yield. Though it may improve other properties, like electrical conductivity in case of carbon materials for batteries or supercapacitors and magnetic properties in case of magnetic-activated carbons for wastewater treatment.

Pyrolysis of hydrochars derived from biogas digestate (corn silage and cow manure) was studied by Garlapalli et al. (Garlapalli et al., 2016). They obtained yields of pyrolyzed (600 °C) hydrochars in the range of 25.4-28.1 wt.%, while pyrolysis of initial digested resulted in the yield of 30.3 wt.%. They studied N₂ adsorption for hydrochar produced at 260 °C and then pyrolyzed at 800 °C. The S_{BET} (63.4 m² g⁻¹) for this char was lower compared to digested pyrolyzed at this same temperature (161.6 m² g⁻¹). Wang et al. (Wang et al., 2019) reported pyrolysis of hydrochars produced from sewage sludge (municipal wastewater treatment plant). Unfortunately, they expressed the pyrochar yield only in the one-step pyrolysis, where hydrochar is the input material (similar to scatters in Fig. 1A) instead of the yield calculated based on both processes. Therefore, they observed a similar trend that was obtained in this study, (higher temperature of hydrothermal conversion sharply increased the pyrolysis yield). The study of Wang et al. (Wang et al., 2019) also reported the N₂ adsorption isotherms, they found that hydrothermal pretreatment caused an increase in the surface area and the S_{BET} for hydrochar (47.0 m² g⁻¹) produced at 220 °C and then pyrolyzed at 500 °C was higher than pyrochar (22.2 m² g⁻¹) from sewage sludge obtained at 700 °C. Both groups used feedstocks with significantly higher ash contents compared to BSG (4.7 wt.%), i.e., 10.7 wt.% for digestate and 46.6 wt.% for sewage sludge (Garlapalli et al., 2016; Wang et al., 2019). It should be mentioned that both research groups choose only one

233 pyrolyzed hydrochar for surface area determination and in both cases the hydrochars were
234 produced at the highest tested temperatures (i.e., 260 and 220 °C, respectively). The results in this
235 study showed that the highest surface area was obtained for the hydrochar produced at the mildest
236 HTC condition (180 °C) and then pyrolyzed at 600 °C (Table 1).

4.3. Wet and dry conversion

In recent times, comparing wet and dry conversions has attracted a lot of scientists' attention (Bach and Skreiberg, 2016; Libra et al., 2011; Liu and Balasubramanian, 2014), mainly due to the possibility to avoid energy-intensive thermal drying before HTC and spread the range of waste biomasses used for biorefinery purposes. Herein, high-temperature HTC showed better results than low-temperature pyrolysis. Under the tested condition, the mass yield of HTC-260 (38.36 wt.%) was higher than Py-400-BSG (33.05 wt.%). HTC-260 showed higher carbon yield, higher carbon content, as well as lower ash, compared to pyrochars. HTC-260 had much higher volatiles (54.63 wt.%) compared to Py-400-BSG (28.26 wt.%); as a result, hydrochar showed the highest HHV (28.37 MJ kg⁻¹). It can be beneficial for application in electricity generation, because of the energy densification, vigorous reactivity, and proper combustion characteristic (Bach and Tran, 2015; Yang et al., 2016). On the other hand, it should be mentioned that BSG contains significant quantities of nitrogen, which is an important drawback in solid fuels. Since the combustion of N-rich fuel generates large amounts of greenhouse gases in the form of NO_x, for that reason application of BSG as solid fuel is strongly not recommended.

Last but not least, it should be considered that HTC requires elevated pressure above water saturation pressure to keep water in a liquid state and avoid the heat loss of water vaporization. In the case of HTC at 260 °C, the pressure in the reactor should be above ca. 47 bar. Such high pressure increases the investment costs significantly for the reactor as well as auxiliary equipment. In continuous processing, the high-pressure feeding and discharging slurry systems may be challenging (Bach and Skreiberg, 2016) due to preferably high solid biomass load. Therefore, HTC requires much more advanced solutions compared to relatively simple pyrolysis. However, by reducing the temperature of HTC to 180 °C, the operating pressure can be decreased

and kept around 10 bar. Such a change may attract industry for the application of cascaded low-temperature HTC and pyrolysis to produce biowaste derived carbons.

5. Conclusion

The common drawback of wasted feedstock streams is high moisture content. Therefore, the application of those streams in thermochemical conversion is sharply limited. To overcome this drawback, we propose the novel cascaded HTC followed by pyrolysis process. This study aimed to investigate the influence of HTC on the pyrolysis of BSG. The results showed that the two-step process at the selected process condition improved the physicochemical properties of the final char. Low-temperature HTC before pyrolysis at 600 °C resulted in higher carbon content and larger surface area compared to one-step pyrolysis of BSG. Additionally, pyro hydrochars were characterized by lower ash content. The key results were that low-temperature HTC followed by pyrolysis kept the similar mass yield and carbon yield as one-step pyrolysis of BSG. These findings may increase the interest in the coupling of both thermochemical processes due to the possibility to design tailor-made carbon materials, thanks to the various reaction mechanisms that occur during individual processes. However, further studies are necessary to investigate if the integration of HTC and pyrolysis may improve overall energy efficiency as well as analyze the economic feasibility of the novel route for producing carbon materials. One can also be interested in the study of other potential feedstocks for the cascaded process in case of improved properties and process efficiency.

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Appendix A

Fig. A1. Adsorption and desorption isotherms for pyrochars produced at 600 °C.

Fig. A2. FT-IR for pyrolyzed materials at A 800 °C and B 1000 °C

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