Sustainable production of solid biofuels and biomaterials by Microwave-Assisted, Hydrothermal Carbonisation (MA-HTC) of Brewers' Spent Grain (BSG)

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ABSTRACT: This work addresses the management of Brewers' Spent Grain (BSG) using a state-of-the-art, microwave-assisted, hydrothermal carbonisation (MA-HTC) process, for the

production of hydrochar, i.e., a renewable solid biomaterial with many industrial applications. For the first time, a detailed relationship has been established between the processing conditions and the properties of the hydrochar via a thorough physicochemical characterisation. The experimental results revealed that the temperature (180-250 °C) and reaction time (0- 2h) used in the MA-HTC process exerted a significant influence on the yield and properties of the hydrochar. An increase in these variables (process severity) diminished the hydrochar yield. However, such increments were beneficial to enhance the fuel properties of this product, as the proportions of O and C decreased and increased, respectively. As a result, this process was capable of transforming up to 47% of the original BSG into a high energy hydrochar with a calorific value of 32 MJ/kg. The characterisation of the hydrochar revealed that it was a mesoporous, hydrophilic, rough material, containing several cavities and oxygen functionalities on the surface. These features not only provide the hydrochar with a high aromatic character but also are fundamental for its potential applicability as a bio-adsorbent material. An increase in the MA-HTC severity augmented the amounts of aliphatic and aromatic structures in the hydrochar as well as the roughness and the presence of cavities, thus highlighting the excellent flexibility of the process. Therefore, these promising results, together with the energy-efficient and bespoke nature of the MA-HTC process, which substantially reduces the reaction temperature and processing times in comparison to standard carbonisation procedures reported to date, represent a step-change not only for the production of biofuels and biomaterials but also for the management of BSG.

KEYWORDS: Brewers' Spent Grain, microwaves, hydrothermal carbonisation, biofuels, biomaterials.

INTRODUCTION

Brewers' Spent Grain (BSG) is a by-product made in large quantities (around 90 million tons per year worldwide), from the mashing and filtration of malting grains, in the manufacturing of beer (100 L of brewage leads to the formation of 45 kg of BSG).¹ This by-product comprises around 30 wt.% of solid matter, consisting of barley malt grain husks, containing some of the hulls and seed coat layers, together with 70 wt.% of moisture (principally H₂O). This high water content promotes microbial growth, thus hampering BSG transportation, storage and disposal.² As such, the efficient and responsible management of BSG is a critical issue, and novel procedures must be established to this end.

In this regard, over the past few years, three approaches have been considered. The first includes the use of BSG as a co-feeding solid or promotor in different areas, such as biomedicine,³ brick⁴ and paper⁵ manufacturing and adsorbents for Cd⁶ and Cr⁷. The second comprises the utilisation of BSG in the chemical and food markets without valorisation, whilst the third relies on the use of thermochemical and biological transformations. Biological routes included the productions of biodiesel, H₂, butanol, ethanol, lactic acid and xylitol by fermentation of the saccharide matter in BSG; however, the utilisation of the lignin fraction was not addressed.⁸ On the contrary, the use of thermochemical processes provides the possibility of furnishing a broad range of biofuels, biochemicals and bio-materials from the whole BSG, including the cellulose, hemicellulose and lignin contents. In particular, hydrothermal treatments (HTT), including both hydrothermal carbonisation and liquefaction, are considered state-of-the-art technologies to transform wet biomass into these commodities.⁹ Besides, HTT offer several advantages over other routes, such as the triple role of the water in the process, as it performs as the solvent, reagent and catalyst; the use of lower temperatures in comparison to other routes, such as pyrolysis and/or gasification (200-400 °C vs

450-750 °C) and, the possibility of employing wet biomass without any drying step.¹⁰ Between these, hydrothermal carbonisation (HTC) is intended to transform biomass into a high value-added solid material, known as hydrochar, with many potential industrial applications.

Hydrochar is a solid bio-material with improved physicochemical and fuel properties than the original biomass. The chemical composition, surface properties and morphological characteristics of this solid are determined by the source of biomass and the technology and processing parameters used during its production.¹¹ Specifically, the temperature and reaction time are the most influential variables affecting the physicochemical properties of hydrochars produced from lignocellulosic biomass.¹² For instance, works addressing the hydrothermal carbonisation of sugar cane and peanut shells¹³ and hazelnut shells and olive wastes¹⁴ revealed that the temperature and time were the processing conditions with the most substantial impact on the physicochemical properties of the hydrochars produced. Regarding the outcomes of the processing parameters on the physicochemical properties of this material, Gao et al.¹⁵ reported that prolonging the duration of the process increased the number of microspheres created on the surface of hydrochar.

Despite the fact that the effect of the conditions is relatively well understood, the actual mechanism for the transformation of biomass into hydrochar is quite complicated. This is a result of the diverse and complex chemical structure of biomass, primarily comprising three main structural constituents (cellulose, hemicellulose and lignin). Given this, several routes have been discussed in the literature explaining the formation of hydrochar from either carbohydrates or lignin. On the one hand, Dinjus et al.¹⁶ considered the formation of hydrochar from lignin-based materials via a solid direct conversion of biomass (polyaromatic char). On the other, Sevilla and Fuertes¹⁷ proposed the formation of hydrochar from carbohydrates (cellulose and hemicellulose) via polymerisation and/or condensation of dissolved monomers resulted from the decomposition

of the biomass carbohydrate content.^{17, 18} In both routes, the final product is a solid material with a polyaromatic structure, consisting of spherical microparticles with a hydrophobic core and hydrophilic shell.¹⁹

These chemical features and renewable nature convert the hydrochar produced from biomass into an excellent not only energy carrier (solid biofuel) but also biomaterial for different applications, such as bio-adsorbent for contaminated soil²⁰ and/or polluted water.²¹ Nonetheless, the direct applicability of the hydrochar produced by HTC as a bio-material is not always possible. This is accounted for by its relatively low surface area, particularly if compared to that of activated carbons; though, it is also slightly inferior to that of the biochars produced from the pyrolysis of biomass.²²⁻²⁴ However, this drawback can be surpassed by modifying the structure of the hydrochar after production, leading to a substantial improvement in the surface properties of this material, which allows us to achieve surface areas as high as those of activated carbon.¹⁹ Such modification can be easily achieved via a chemical activation using KOH, NaOH and/or H₃PO₄,^{25, 26} due to the occurrence of several oxygen functionalities, principally oxygenated, on the surface of the hydrochar.

After activation, hydrochars are outstanding bio-materials for many applications. For example, the hydrochar produced from biomass was used for capturing methylene blue and Cu (II) from sewage water,²⁷ and CO₂ from combustion gas.²⁸ Furthermore, Sevilla et al.,²⁹ Parshetti et al.³⁰ and Vieillard et al.³¹ reported that after activation, the hydrochar obtained from different feedstocks was an excellent material for CO₂ capture, reaching in some cases, an adsorption capacity of 3.71 mmol/g. Despite these promising applications, there are very few studies in the literature addressing the production of hydrochar (or biochar) from BSG using either HTT or any other technology. Gonçalves et al.³² obtained biochar from BSG by pyrolysis and studied its application

as a bio-adsorbent for iodine and methyl blue. However, a substantial amount of energy was required in the pyrolysis step due to the high water content of BSG. In another work, Wikberg et al.³³ obtained a hydrochar from BSG by hydrothermal treatment. Nevertheless, they focused on energy purposes, and only the elemental composition and the Higher Heating Value (HHV) of the hydrochar were reported, without providing a detailed analysis on the physicochemical and textural properties of this material for other applications. These publications provide valuable insights into the production of hydrochar by HTC. However, one of the significant challenges of this technology is the use of long reaction times (up to 7 h)³³, which might represent an energy barrier for the profitability and sustainability of the process.

Given these drawbacks, a possible solution to improve the energetic aspects of the process might be the use of microwave technology. This methodology allows the conversion of electromagnetic radiation into heat energy within the objective material, and it is contemplated as one of the most favourable options to achieve an energy-efficient thermochemical valorisation of biomass.^{34, 35} In particular, microwave-assisted processes use lower temperatures in comparison to their counterparts using conventional heating, which is beneficial for the energy and controllability aspects of any process. Besides, considering the high effectivity of water to absorb microwave energy, the use of microwave-assisted hydrothermal treatments is seen as an excellent option. As such, the utilisation of microwave technology to run chemical reactions at hydrothermal conditions is considered state-of-the-art technology. However, works employing microwave-assisted pressurised reactors to conduct hydrothermal treatments in general^{8, 36, 37} and hydrothermal carbonisation, in particular, are very scarce.

In particular, Elaigwu and Greenway³⁸ addressed the HTC of lignocellulosic biomass comparing conventional and microwave-assisted heating. Such comparison was conducted at 200 °C, using a

reaction time between 120 and 240 min for the former and 5 and 20 min for the latter technology. The comparative assessment revealed that use of microwave-heating reduced the reaction time dramatically from 240 to 20 min. Besides, Dai et al.³⁹ established a correlation between the hydrochar produced from bamboo using conventional and microwave-assisted heating. The experimental results revealed that the use of microwave-assisted heating led to a substantial reduction in the reaction time accompanied with a considerable improvement in the fuel properties of the hydrochar produced. In a previous work, we developed a new microwave-assisted hydrothermal liquefaction (MA-HTL) process for the valorisation of BSG.⁸ This route was an excellent technology for the simultaneous production of biofuels (biocrude and hydrochar) and higher-value-added chemicals (oligosaccharide water solutions) in a sole process. Nevertheless, none of these studies have analysed the impact of the processing reaction parameters on the physicochemical properties of the hydrochars produced, and more work is still necessary for the development, improvement and commercialisation of this technology.

Herein, this work addresses the valorisation and management of BSG by microwave-assisted hydrothermal carbonisation (MA-HTC), for the conversion of this beer by-product into a hydrochar with many industrial applications in the energy and material markets. For the first time, this investigation thoroughly examines the detailed impact of the most influential processing conditions (temperature and reaction time) on fundamental fuel and physicochemical properties of this solid, determined by means of an exhaustive characterisation of the material. Given the lack of works covering the production and possible applications of hydrochar produced from BSG, along with the limited amount of works addressing the hydrothermal carbonisation of biomass under microwave-assisted heating, this work exemplifies a step forward in this field.

EXPERIMENTAL

Feedstock characterisation

MAHOU San Miguel Alovera (Guadalajara, Spain) provided the BSG used in this work. The water content (75 wt.%) of the material was removed in a freeze dryer to prevent the degradation of the feedstock during the investigation. The dried BSG was characterised by ultimate, proximate and fibre analyses, ash and lipids content contents and calorific value. The detailed methodology and characterisation are fully reported in our previous publication.⁸ Very briefly, the dried BSG consisted of 63 wt.% volatiles, 25 wt.% fixed carbon, 1.4 wt.% moisture and 8 wt.% ash (principally Ca, P and S). The fibre analysis revealed that the relative amounts of cellulose, hemicellulose, lignin, proteins and lipids in the dried solid were 24 wt.%, 16 wt.%, 25 wt.%, 24 wt.% and 5 wt.%, respectively. Besides, it contained a relative amount of C, H, N and O of 50 wt.%, 7 wt.%, 4 wt.% and 39 wt.%, respectively, and had a HHV of 21 MJ/kg.⁸

Reaction set-up and experimental procedure

The experiments were conducted in a Milestone SynthWave, microwave-assisted, pressurised reactor described in detail previously.⁸ Very briefly, the rig consists of a 1 L water-cooled high-grade stainless steel, high temperature and pressure (300 °C and 199 bar) batch reactor, with a magnetron connected by a waveguide generating microwave radiation. The pressure vessel is made of special stainless steel and is locked with a clamping device. The microwave power is controlled with the aid of a PID controller. At the same time, the internal temperature and pressure are respectively monitored and controlled by a thermowell and a pressure sensor, both placed internally. Dynamic mode operation, wherein the power was regulated to attain the reaction temperature as rapidly and precisely as possible, was used for the MA-HTC experiments. At full

power, the microwave produces nearly 1800 W of microwave energy at the frequency of 2450 MHz.

For the experiments, the reactor was loaded with 20 g of BSW along with 400 mL of deionised water. Subsequently, it was purged with N₂ and pressurised with a bespoke amount of N₂ to reach the required pressure at reaction conditions. For all the runs, the reaction conditions were achieved after a ramp time (from c.a. 25 °C) of 15 minutes, which corresponds to a heating rate of 11-15 °C/min. The experiments were conducted at 50 bar, studying the influences of the reaction temperature and time, which varied between 180 and 250 °C and 0 and 2 h, respectively. After the reaction, the temperature was decreased. The microwave cavity is water-cooled and was connected to a chiller, which contains water at around 5 °C, to reduce the temperature as quickly as possible. The microwave own cooling program was used in this step to drop the temperature and experimental observations reveals that at these conditions the temperature decreased from the experimental conditions to around 60 °C at a rate of c.a. 12 °C/min.

Then, the pressure was released and the reaction products (bio-oil, aqueous soluble products, hydrochar and gas) were recovered and quantified. The gas yield was determined gravimetrically by weighing the whole reaction vessel prior to (containing the BSG water and stirrer bar) and after (once the gas had been released, and therefore including the bio-oil, hydrochar, water and stirrer bar only) each run. The production of H₂ and CH₄ is not preferential thermodynamically under the processing conditions tested and the gas phase essentially comprises CO₂^{40, 41}. The hydrochar was dried overnight at 105°C and quantified gravimetrically. The bio-oil was separated from the water employing a two-step liquid-liquid separation.⁴² Then, a rotary evaporator was used to remove the solvents and recover the bio-oil, which was finally dried under vacuum and weighed. The gas and

aqueous yields were calculated gravimetrically. The detailed experimental procedure is fully described in our previous investigation.⁸

Physicochemical characterisation of the hydrochar

The hydrochar produced during the MA-HTC experiments was characterised by elemental and thermogravimetric analyses, calorific value, Fourier transform infrared spectroscopy (FTIR), Raman Spectroscopy and Scanning electron microscopy (SEM). Elemental analyses were carried out in a LECO CHNS-932 Elemental Analyser. These results were used to calculate the O/C and H/C mass ratios (Eq. 1 and 2) of the hydrochar and used in the Van Krevelen diagram.

$$O/C = \frac{M_C \cdot O\%}{M_O \cdot C\%} \quad (\text{Eq.1})$$

$$H/C = \frac{M_C \cdot H\%}{M_H \cdot C\%} \quad (\text{Eq. 2})$$

M_C , M_O and M_H are the molecular masses of carbon, oxygen, and hydrogen, respectively.

The Higher Heating Value (HHV) of the hydrochar was measured employing an automatic calorimeter (6400 Parr instrument company). From this analysis, the Energy Densification (D_E) and Energy yield (Y_E) were calculated using Eq. 3 and Eq. 4, respectively.

$$D_E = \frac{HHV_{hydrochar}}{HHV_{raw\ material}} \quad (\text{Eq. 3})$$

$$Y_E(\%) = Yield_{Solid} \cdot D_E \quad (\text{Eq. 4})$$

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analyses were recorded in a thermogravimetric analyser SDT Q00 (TA Instruments). These analyses were done under a N_2 atmosphere, raising the temperature from room temperature to 800°C, at a rate of 20 °C/min. The moisture content was determined by heating the samples to 105°C for 24 h. The fixed carbon and volatiles were calculated from the TGA analysis. The ash content of the samples was determined

conducting the TGA in an oxidising atmosphere using an air stream. The functional groups were analysed by Fourier transform infrared spectroscopy (FTIR) in an IR Affinity-15 (Shimadzu) spectrophotometer in the range of 400–4000 cm^{-1} . Raman spectra were recorded using a Renishaw InVia Reflex spectrometer, while Scanning electron microscopic (SEM) images were taken by a ZEISS GeminiSEM 500 scanning electron microscope, operating from 3 pA to 20 nA. The BET surface area of the samples was determined in a QUANTACHROME NOVAtouch LX2 apparatus, using N_2 as the adsorbate at 77 K. For this, the samples were compacted in pellets by adding a small amount of deionised water. This water was removed prior to the analyses in an oven at 110 °C for 24 h to make sure all the water was removed from the pellets. Pore size and pore volume analyses were determined by the Density Functional Theory (DFT). Although there are many different approaches to determine the pore volume, methods such as BJH and HK do not give a clear picture of micropores or mesopores. On the contrary, the DFT method resolves both micropores and mesopores and is supported by the 77 K N_2 adsorption isotherms in carbonaceous materials (similar to the hydrochar studied) characterised by slit-shaped pores. This method has been widely used for the characterisation of micro and meso carbonaceous pores^{43, 44} and therefore was used in this work.

Energy measurements and process effectiveness

The Energy consumption of the microwave unit was measured with an Energenie ENE007 power meter connected between the microwave unit and the electric plug. At the same time, the theoretical energy input was estimated as the amount of energy required to heat the feedstock (20 g of BSG and 400 mL of water) to reaction conditions using the calorific value and the total amount of water. These data were used to calculate the microwave energy yield (Mw E. yield), theoretical

process yield (Process E. yield) and microwave efficiency (Mw Efficiency) using Eq. 5, 6 and 7, respectively.

$$Mw\ E.yield(\%) = \frac{Bio-oil\ (kg) \cdot Bio-oil\ HHV\ (MJ \cdot kg^{-1}) + Hydrochar\ (kg) \cdot Hydrochar\ HHV\ (MJ \cdot kg^{-1})}{Total\ Energy\ consumption\ (MJ)} 100 \quad (Eq. 5)$$

$$Process\ E.yield(\%) = \frac{Bio-oil\ (kg) \cdot Bio-oil\ HHV\ (MJ \cdot kg^{-1}) + Hydrochar\ (kg) \cdot Hydrochar\ HHV\ (MJ \cdot kg^{-1})}{Theoretical\ total\ energy\ input\ (MJ)} 100 \quad (Eq. 6)$$

$$Mw\ Efficiency\ (\%) = \frac{Mw\ E.yield\ (\%)}{Process\ E.yield\ (\%)} 100 \quad (Eq. 7)$$

RESULTS AND DISCUSSION

Hydrochar yield and fuel properties

The effects of the temperature (180 and 250 °C) and reaction time (0 and 2 h) were analysed in terms of their impact on the distribution of the overall products (hydrochar, bio-oil, aqueous phase and gas), and the elemental and proximate analysis and fuel properties of the hydrochar produced. These data are recapped in Table 1. The results indicate that the MA-HTC processing conditions exert a significant influence on the overall distribution of reaction products and the physicochemical and fuel properties of the hydrochar. In particular, increasing the reaction temperature from 180 to 250 °C and/or prolonging the time from 0 to 2 h decrease the hydrochar yield at the expenses of the gas, bio-oil and aqueous fraction yields. These variations also lead to decreases in the proportion of O and increases in the relative amount of C of the hydrochar, which enhances its HHV. These developments might be the consequence of the beneficial impact of the temperature and reaction time (more energy applied and more prolonged exposure of the biomass to microwave heating) on the process, which endorses the spread of deoxygenation reactions, mainly dehydration and decarboxylation, leading to increases in the fixed carbon and HHV of the material along with decreases in its volatile content.^{15, 45} Besides, the impacts of the temperature and reaction time are also reflected in the ash content. In this case, the hydrochar obtained at the

highest temperature and longest reaction time shows a considerable reduction in the ash content compared to that of the raw feedstock. This phenomenon accounts for the presence of water in the MA-HTC process, which helps to leach these inorganic species from the biomass into the liquid product stream. Generally, this takes place by an acid solvation mechanism, involving the solubilisation and leaching of inorganic compounds, thus reducing the overall ash content of the solid product.^{23, 46}

Table 1. Yields to products and physicochemical and fuel properties of the hydrochar produced at different temperatures and reaction times

Run	BSG	1	2	3
T (°C)	-	180	250	250
t (h)	-	2	2	0
Overall Products distribution				
Hydrochar yield (%)	-	46.92	35.46	43.69
Bio-oil yield (%)	-	5.23	7.65	6.85
Aqueous yield	-	24.90	25.37	30.21
Gas yield	-	22.94	31.52	19.26
Hydrochar Elemental Analysis				
C (wt.%)	50.28	59.30	71.14	58.20
H (wt.%)	6.37	7.38	7.01	7.26
N (wt.%)	3.93	2.44	3.45	2.64
O (wt.%)	39.17	30.87	18.38	31.59
O/C (mol/mol)	0.58	0.39	0.19	0.41
H/C (mol/mol)	1.52	1.49	1.18	1.50
Proximate analysis and Fuel properties				
HHV (MJ/kg)	20.95	26.50	31.75	26.82
Moisture	1.38	3.29	1.89	2.86
Ash	7.98	7.71	3.45	7.29
Fixed carbon (wt.%)	24.41	26.13	45.86	29.27
Volatiles (wt.%)	66.23	62.87	48.80	60.58
Fuel ratio ^a	0.36	0.41	0.94	0.48
Energy densification	-	1.26	1.51	1.28
Energy yield (%)	-	59.11	53.54	55.92
Process Energy assessment				
Energy consumption (kWh)		0.096	0.132	0.124
Mw E. yield (%)		73.95	71.16	59.73
Process E. yield (%)		98.61	88.89	70.88
Mw Efficiency (%)		74.99	79.17	84.27

^a (Fixed carbon/volatile matter)

Besides, the processing conditions do not modify the percentage of H, while the N content is also similar in all samples, but lower than in the raw material. This indicates that deamination reactions take place to a substantial extent during the MA-HTC process. Accordingly, the amino groups in proteins are broken, thus releasing nitrogen in the form of NH_3 or NO_x . As a result, the energy densification and energy yield increase with uprisings the temperature and/or enlarging the reaction time. For example, the hydrochar obtained using the highest temperature (250 °C) and the longest reaction time (2 h) has a HHV of 32 MJ/kg, i.e., between lignite (29.6 MJ/kg) and coke (33.7 MJ/kg). This corresponds to an energy yield of 51% and confirms that this material could be used for energy applications. These results point out the inherent advantages of this MA-HTC process. In particular, not only the HHV of the hydrochar (32 MJ/kg) is higher than that reported by Wikberg et al.³³ (30 MJ/kg) using conventional heating at 260 °C, but also the duration of the process decreases from 7 h to a maximum of 2 h with the application of microwave technology.

The total electric energy needed for the MA-HTC of BSG (involving both electricity to microwaves and microwaves to thermal conversions) varied between 0.096 and 0.132 kWh depending on the conditions, which corresponds to energy requirements of 17, 24 and 22 MJ (4.7, 6.7 and 6.1 kWh) per kg of BSG for run 1, 2 and 3, respectively. Besides, the Mw E. yield varied between 60 and 74%. In comparison, the Theoretical Process E. yield shifted between 71 and 98%, thus highlighting the high efficiency of this MA-HTC process for the production of an energy-dense hydrochar using moderate temperatures and very short reaction times. The combination of these data (Mw E. yield and Process E. yield) reveals the good Mw efficiency (75-85%) of this MA-HTC process. This high efficiency, along with the substantial reduction in the reaction time in comparison to the HTC of BSG using conventional heating (from 7 down to 2 h)³³ are paramount for the management of novel BSG. Also, it must be borne in mind that the process is still at an

early step of development and that a lab-scale microwave unit was used for this proof of concept. These lab-scale microwaves run at 2.45 GHz, which results in a lower electrical efficiency in comparison to that of large-scale industrial microwaves. These latter work at much lower frequencies (896 and 922 MHz), which allow them to attain electrical efficiencies greater than 85%.^{47, 48}

Figure 1 shows a Van Krevelen diagram, plotting the evolutions of the molar H/C and O/C ratios (indicators of the degree of carbonisation) for the hydrochar produced by MA-HTC at different operating conditions, with respect to these ratios in the original BSG. The strength of hydrothermal carbonisation can be attained by the O/C-H/C vector length, and it is substantially influenced by the extension of dehydration and decarboxylation reactions in the process. HTC dehydrations are a result of chemical and physical transformation, via the elimination of hydroxyl groups. As such, the biomass is carbonised, and the O/C and H/C molar ratios decrease. The lowering in the O/C molar ratio indicates the elimination of the carboxyl groups from the extractives, hemicellulose, and cellulose contents in the biomass during the HTC process. At the same time, the decreases in the H/C molar ratios denote the elimination of the hydroxyl groups in the process.

The experimental results show that increases in the temperature or reaction time lead to decreases in the H/C and O/C ratios. These variations are believed to be the result of an increase in the degree of dehydration, decarboxylation and condensation reactions with augmenting the temperature and/or prolonging the reaction time, and are in good agreement with previous studies.^{49, 50} In particular, high H/C and O/C ratios account for the presence of primary biomass macromolecules (i.e., cellulose and hemicellulose), showing a negligible residual biomass decomposition. Low H/C and O/C ratios are typical of more condensed (aromatic) structures.^{11, 12}

As a result of these different transformations, Run 1 and 3 have similar O/C (0.39 and 0.41) and H/C (1.49 and 1.50) ratios. This indicates that the combinations of temperature and time used in these experiments resulted in the same extension of dehydration and decarboxylation reactions. On the contrary, Run 2 has lower O/C (0.19) and H/C (1.18) ratios due to a more significant elimination of the hydroxyl groups in the process. Therefore, at low temperatures and short reaction times (Run 1 and 3), the hydrochar produced resembles the original BSG because under these conditions there is still unreacted cellulose (as will be seen later in the thermogravimetric analysis). In contrast, at elevated temperatures and/or long reaction times (Run 2), the hydrochar has a much lower O/C ratio, which is very close to lignite, due to the progressive depolymerisation of the BSG in the process.

Figure 1. Van Krevelen diagram showing the effect of the operating conditions on the H/C and O/C ratios of the hydrochar.

Thermal properties

Figure 2 shows the thermograph (TG) and derivative thermograph (DTG) analyses for the hydrochar produced at different processing conditions. These analyses reveal that the DTG curves can be divided into three mass loss regions at three specific temperature intervals. The first interval (region I) spans between 0 and 210 °C and take place irrespective of the processing conditions used in the MA-HTC process. This step primarily comprises moisture loss, principally water and low boiling organic matter produced during the process. Region II goes from 210 to 420 °C and corresponds to the degradation of hemicellulose and cellulose, while Region III, occurring between 420 and 700 °C, is mainly attributed to the loss of aromatic compounds. These include lignin along with some condensation products that can be formed during the MA-HTC process, resulting from the degradation and recombination of aliphatic compounds.¹² The shape of the DTG curves depends on the MA-HTC processing conditions. In particular, when the process is conducted at a low temperature and using a short reaction time, only hemicellulose degradation takes place. Conversely, augmenting the severity of the process, i.e., increasing the temperature and/or prolonging the reaction time, the hemicellulose and cellulose contents of BSG disappear, and the hydrochar is principally made up of lignin, proteins, and condensation products.

With regard to the effect of the temperature, when the MA-HTC treatment is conducted at low temperature (180°C), only the hemicellulose fraction in BSG is fully degraded (Figure 2 b). A further increase in the temperature up to 250 °C (Figure 2 c) produces not only the degradation of hemicellulose, but also the cellulose content of the biomass, and a single peak corresponding to lignin appears at 450 °C. Besides, a small shoulder corresponding to the degradation of the proteins appears at around 360 °C. Concerning the effect of residence time, Figure 2d (0 h) displays two distinct peaks in the DTG curve at 240 °C and 350 °C. The former corresponds to condensation

products, while the latter, being very intense, indicates the decomposition of cellulose. Given these data, an increase in the reaction time from 0 to 2 h produces a hydrochar primarily consisting of lignin, proteins and condensation products. As such, an increase in the severity of the process increases the thermal stability of the hydrochar; thus loss of mass is lower at higher temperatures and using longer residence times (71% vs 54%). These results correlate very well with the Van Krevelen diagram described above.

Figure 2. Thermographs and derivative thermographs of the original BSG (a) and hydrochar produced for Run 1 (b), Run 2 (c) and Run 3 (d).

Surface functional groups

The characterisation of the hydrochar by Fourier Transform infrared spectroscopy (Figure 3) shows that irrespective of the processing conditions, it contains a high proportion of oxygenated and aromatic compounds. In particular, the absorption bands appearing between 3000-3600 cm^{-1} , which correspond to the -OH vibration of hydroxyl and carboxyl groups^{16, 51}, are common to all

the samples. Conversely, the intensity of these bands depends on the processing parameters employed in the MA-HTC process. An increase in the temperature and/or reaction time decreases the strength of these bands, thus suggesting that dehydration and decarboxylation are the main reactions taking place during the MA-HTC of BSG.⁵² These results connect very well with the elemental composition and thermal properties of the hydrochar described above.

Figure 3. FTIR spectra of the hydrochar produced at different temperature (a) and time (b).

The comparison between the spectra of the hydrochar produced at different MA-HTC conditions with the spectrum of the raw material (BSG) reveals an increase in the intensity of the bands appearing between 2918 and 2850 cm⁻¹, which accounts for the stress and deformation vibration of the aliphatic C-H bonds. This development might indicate the presence of aliphatic and aromatic structures in the hydrochar, including both the carbonyl band (1699 cm⁻¹) and the bands at 1000-1600 cm⁻¹ corresponding to lignin.^{29, 53} This increase is particularly marked for the band appearing at 1512 cm⁻¹, denoting the vibration of the C=C bond of aromatic rings, thus highlighting the higher aromaticity of the hydrochar in comparison to that of the original BSG. Regarding the effects of the MA-HTC operating conditions, an increase in the temperature and/or

reaction time leads to a decrease in the intensity of the C-O band (1050 cm^{-1}). Such variation is accounted for by the rupture of C-O bonds (ether bonds between cellulose and lignin bonds). This development confirms the progressive depolymerisation of cellulose and hemicellulose, thus augmenting the lignin content in the hydrochar, with increasing the severity of the MA-HTC process. Besides, these superficial oxygenated functional groups aid to functionalisation, this being of paramount importance for the future applicability of hydrochar as a bio-based material in many fields. In particular, the presence of oxygenated functionalities increases the hydrophilic nature of the solid, which is beneficial for many different applications, including adsorption, catalysis¹⁹ and CO_2 capture.⁵⁴

To gain an in-depth insight into the aromatic character of the hydrochar, the solids were analysed by Raman Spectroscopy (Figure 4). The Raman spectra of the hydrochar produced at high temperature and long reaction time ($250\text{ }^\circ\text{C}$, 2h) display two bands at different intensities: D-band at 1360 cm^{-1} (D-diamond or disorder) and G-band at 1587 cm^{-1} (G-graphite), which indicates the presence of sp^2 carbon. On the contrary, when the MA-HTC process is conducted at the same temperature ($250\text{ }^\circ\text{C}$) but using a short reaction time (0 h, blue line) these bands do not appear. These bands reveal the presence of amorphous aromatic carbon structures in the hydrochar, together with a graphite-type ordinate.⁵⁵ The comparison between the Raman spectra of the hydrochar produced at $250\text{ }^\circ\text{C}$ and 2 h (green line) and that of the original feedstock (black line) reveals that the G and D bands only appear in the former solid, thus confirming the higher aromaticity of the hydrochar in comparison to that of the original BSG. In addition, at low temperature ($180\text{ }^\circ\text{C}$, red line), the D and G bands are not present either, while a new band appears at 1540 cm^{-1} . This latter corresponds to the G_R band, which is characteristic of amorphous carbon structures.⁵⁶ This finding seems to indicate that the condensation reactions, leading to the

formation of aromatic structures, do not take place to a significant extent at low temperature. Thus, these results confirm that the aromaticity of the hydrochar increases with augmenting the temperature of the MA-HTC process.

Figure 4. Raman spectra of the hydrochar produced at different temperatures and reaction times.

Surface properties and morphology

Surface properties

Table 2 lists the surface, pore size and volume for the hydrochar produced at different temperatures and reaction times. In general, the porosity of the hydrochar produced from the MA-HTC of BSG is relatively low, and the operating conditions used in the process do not have a substantial impact on the surface properties of this material. In particular, increases in the temperature from 180 to 250 °C or in the reaction time from 0 to 2 h diminish the BET surface area from 3 to 0.4 m²/g or 1 m²/g, correspondingly. This trend is also observed for the external surface area, which includes the non-micro-porous part of the material; i.e., the outermost convex particle surface, including both mesopores and macropores. These variations are accounted for by

an increase in the severity of the process, as the use of high temperatures or long residence times alters the structure of the hydrochar. Under these HTC conditions (250°C and 2h), the water can break the glycosidic bonds in hemicellulose and cellulose, leading to their degradation into monomers. Afterwards, these species condense yielding polymeric particles, which tend to precipitate onto the pores of the hydrochar. On the contrary, the use of a lower temperature (180°C) and/or a shorter residence time (0 h) avoids condensation and re-polymerisation of the water-soluble components, thus resulting in a hydrochar with a better pore structure.¹¹ Such modification takes place due to the breaking and/or obstruction of the porous structure of the material, confirming that high temperatures and long residence times are not favourable for the formation of a porous hydrochar.⁴¹ Besides, the pore size is intensely induced by the reaction temperature used in the MA-HTC process. In particular, an increase from 180 °C to 250 °C decreases the pore size from 11.16 nm to 2.76 nm. On the contrary, an increase in the reaction time does not exert a significant influence.

Table 2. Surface BET, external surface area, pore size and volume of the hydrochar produced at different processing conditions

Run	T (°C)	t (h)	S _{BET} (m ² /g)	S _{ext} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
1	180	2	3.09	2,76	11.16	0.016
2	250	2	0.37	0,12	2.76	0
3	250	0	1.07	0,69	2.76	0.003

Figure 5 shows the N₂ adsorption isotherms for the materials at 77 K. The shape of the isotherm reveals that irrespective of the processing conditions applied in the MA-HTC process, the isotherm of the hydrochar resembles a Type IV profile according to the IUPAC classification.⁵⁷ Besides, the hysteresis loop observed in all the isotherms is related to the capillary condensation taking place in the mesopores (< 2mm) of the solids.

Figure 5. Adsorption isotherms of the hydrochars obtained at different processing conditions.

To gain an in-depth insight into the micro-porosity of the hydrochar, Figure 6 plots the size distribution using a DFT model. This analysis provides handy information for the possible applicability of hydrochars as bio-materials.⁵⁸ For example, the presence of micropores is one of the requirements to use hydrochars for CO₂ capture.²⁸ This analysis reveals that the material produced at low and high temperature (180 and 250 °C) contains an accumulated radius volume between 5 and 9 nm, and between 4 and 6 nm, respectively. These data prove evidence for the presence of mesopores and are in good agreement with the data shown in Table 2. These findings point out that the hydrochar produced by MA-HTC of BSG could be used as an adsorption bio-material after activation.¹⁹

Figure 6. DFT model showing the pore sizes distribution of the hydrochar obtained at different conditions. $dV(r)$ shows the volume derivative of the pore radius.

Morphology

Figure 7 shows the morphology, determined by SEM, of the original BSG and the hydrochar obtained at different processing conditions. The comparison between the original BSG and the hydrochar reveals that the MA-HTC leads to substantial changes in the surface morphology of the solid phase. The hydrochar produced at low temperature and/or using short reaction times consists of a rough material containing several cavities on the surface, accounting for the decomposition of hemicellulose and cellulose. The roughness acquired during the MA-HTC process is more intense when the severity of the MA-HTC process increases, probably due to the more substantial decomposition/depolymerisation of the material, as described earlier. When the MA-HTC process is conducted at a high temperature and/or using a long reaction time, not only the decompositions of cellulose and hemicellulose take place, but also the partial degradation of lignin (owing to its higher thermal stability) occurs to a substantial extent, thus increasing the roughness of the material.²⁴ Besides, increasing the severity of the process promotes the elimination of gaseous

molecules such as CO, CO₂, CH₄ and/or steam, which also increases the rugosity of the solid material.

Figure 7. SEM images of the original BSG and the hydrochar produced at different processing conditions: Effect of the reaction time (Run 3 vs Run 2) and temperature (Run 1 vs Run 2).

CONCLUSIONS

This work carefully explores the conversion of Brewers' Spent Grain (BSG) into hydrochar via an energy-efficient, microwave-assisted, hydrothermal carbonisation (MA-HTC) process. In particular, the influence of the temperature (180-250 °C) and reaction time (0-2 h) on the yield and key physicochemical properties of the hydrochar has been thoroughly described. The processing conditions not only influence the hydrochar yield but also exert a significant impact on the physicochemical properties of this product. In particular, this process was capable of transforming between 36 and 47% of the original BSG into a hydrochar with excellent features for energy and industrial biomaterial applications, (53-59% of energy yield was recovered and the fuel ratio

improved up to 0.94), using lower temperatures and much shorter reaction times than current technologies reported to date. The experimental results revealed that it is necessary to strike the right balance between the quantity and quality of the hydrochar. In particular, an increase in the reaction temperature and/or time (process severity) diminished the hydrochar yield; however, these variations were beneficial to enhance the fuel properties of this product, as the proportions of O and C decreased and increased, respectively, via dehydration and decarboxylation reactions. This improved the HHV of the hydrochar up to 32 MJ/kg (twice times higher than the original BSG). The characterisation of the hydrochar revealed that it consists of a mesoporous, hydrophilic, rough material, containing several surface cavities, with different oxygen functionalities. These characteristics, related to the processing MA-HTC conditions, provide this solid biomaterial with an aromatic character. An increase in the severity of the process led to increases in the proportions of aliphatic and aromatic structures in the hydrochar compared to the original BSG. Also, its roughness, as well as the presence of cavities augmented when the severity of the process increased. These features are fundamental for the potential applicability of hydrochar as a biofuel and/or an advanced biomaterial. Therefore, these promising results, together with the energy-efficient character and bespoke nature of this MA-HTC process, represent a step-change not only for hydrochar production but also for the valorisation and management of BSG.

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