HTC of Wet Residues of the Brewing Process: Comprehensive Characterization of Produced Beer, Spent Grain and Valorized Residues

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Abstract: Steady consumption of beer results in a steady output of residues, i.e., brewer's spent grain (BSG). Its valorization, using hydrothermal carbonization (HTC) seems sensible. However, a significant knowledge gap regarding the variability of this residue and its influence on the valorization process and its potential use in biorefineries exists. This study attempted to fill this gap by characterization of BSG in conjunction with the main product (beer), taking into accounts details of the brewing process. Moreover, different methods to assess the performance of HTC were investigated. Overall, the differences in terms of the fuel properties of both types of spent grain were much less stark, in comparison to the differences between the respective beers. The use of HTC as a pretreatment of BSG for subsequent use as a biorefinery feedstock can be considered beneficial. HTC was helpful in uniformization and improvement of the fuel properties. A significant decrease in the oxygen content and O/C ratio and improved grindability was achieved. The Weber method proved to be feasible for HTC productivity assessment for commercial installations, giving satisfactory results for most of the cases, contrary to traditional ash tracer method, which resulted in significant overestimations of the mass yield.

Keywords: hydrothermal carbonization; hydrochars; beer; brewers spent grain; pyrolysis

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1. Introduction

Beer is a beverage which can be characterized by a reasonably steady consumption in OECD (Organization for Economic Co-operation and Development) countries [1]. As the OECD consists of developed countries, where a reasonably steady financial situation of citizens can be reasonably assumed, it seems reasonable to assume a steady output of residues, such as spent grain, as a consequence of this consumption. Currently, this residue is mainly used as fodder in agriculture [2].

However, for craft breweries located in big cities, disposal becomes more problematic [3]. There are also attempts to enrich food products with spent grains. Thus far, there have been trials with sausages [4] and bread [5]. However, consumers reported that such products represent a fiber aftertaste [6]. However, this is limited only to the relatively close vicinity of a brewery, due to relatively high moisture content, that could range between 70% up to 78% 70% [7–9]. Biological activity of these residues makes long term storage difficult. The literature reports ongoing work on various new ways of using BSG, including extraction of polyphenols [10,11], other anti-oxidants [12,13], functional cardioprotective lipids for pharmaceutic use [14], proteins [15], fodder for edible insects [16], material for disposable trays [17], natural rubber modifier [18], as well as feedstock for production of pigments [19] and biochar, for subsequent use as soil amendment [20] or sustainable material for electrodes [21].

The potential use of this residue as a fuel has been suggested by several authors so far [7–9,22,23]. The relatively high initial moisture content of spent grain makes hydrothermal valorization techniques the most sensible choice [8,9]. Hydrothermal carbonization (HTC), also known as wet torrefaction, is a valorization process suitable for a range of low-quality solid biomass, especially with high initial moisture content [24,25]. Process temperature, reported in the literature, usually ranges between 180 °C and 260 °C [25–30]. As the process takes place in subcritical water, pressure has to be higher than saturation pressure of water for specific temperature [25–30]. In these conditions water behaves as a non-polar solvent and its ionic constant increases significantly [31]. A multitude of concurring reactions takes place during HTC and a multitude of different products is obtained as a result [25,27]. Firstly, the biomass is degraded by hydrolysis to a vast number of different monomers and oligomers [25] as well as some intermediates [24,25]. In general, the rate of hydrolysis is diffusion-controlled [32]. Therefore, the limitation of transport phenomena is an important factor, especially taking into the account the complexity of fibrous structure different for various types of biomass [32]. Therefore, hydrolysis can be enhanced by the overall increase in the process temperature [33–35]. Hydrolysis is followed by dehydration and decarboxylation [24,25,36]. Dehydration decreases the number of OH groups [25]. Colloidal structures are destroyed, thus decreasing the number of hydrophilic groups and promoting the formation of gases (mainly CO_2) [27]. CO can also be detected, along with CH_4, and H_2 for the case of catalytic processes [33,34]. The decrease in the amount of hydroxyl groups is the cause of decreased O/C ratio of solid products. The amount of carboxyl (COOH) and carbonyl (C = O) groups is decreased, which attributes to the decreased O/C ratio of the solid product [25]. This is followed by polymerization and aromatization [24,25]. A decrease in the number of OH groups is crucial in making hydrochars hydrophobic [37] and enhancing dewatering by mechanical means [25,38]. Moreover, grindability of the processed biomass can be significantly enhanced [39]. Therefore, HTC can be considered as a prospective valorization process for low quality biomass, especially when wet biomass is concerned as a potential feedstock for biorefineries [40–45] or as a component of high quality solid biofertilizers [44,46,47].

Performance of the HTC process is typically determined directly, by means of mass yield, energy yield and energy densification ratio [24,27,41–43,48]. Recently some studies attempted using an indirect method for this purpose [8], originally developed for production of biochar [49]. The use of an indirect method is tempting, especially that it does not require to check the mass of the whole batch after HTC, which could be especially cumbersome and impractical for future industrial-scale installations. However, more research is needed to confirm the suitability of this method for assessment of the productivity of the HTC process in general, as well as specifically for its use for the spent grain.

Drying of BSG was investigated by Arranz et al. [50]. The study showed that significant drying time, exceeding 100 min is required to remove 80% of the original moisture [50]. Obtained effective diffusities were significantly lower than those reported for olive pomace, making BSG a much more challenging material in terms of its drying [50]. Dudek et al. [51] investigated use of BSG as a feedstock for anaerobic digestion (AD), as well as using BSG torrefaction as a mean to produce an AD additive [51]. The information available in the published literature on hydrothermal carbonization of brewer's spent grain (BSG) is not extensive. Jackowski et al. performed a gas chromatography–mass

spectrometry (GC-MS) analysis of the liquid by-product of the HTC of spent grain and suggested its utilization in the anaerobic digestion process [8]. Arauzo et al. studied the effect of hydrothermal carbonization of the spent grain from a big scale brewery and noticed an improvement in fuel properties, such as increased higher heating value (HHV) and decreased ash content (for high water: biomass ratios) [9]. The study also concluded that low temperatures of the HTC process are suitable, due to the high content of hemicellulose in the feedstock [9]. Poerschmann et al. [52] observed that phenols, benzenediols, and fatty acids are released from bound lipids during the HTC process. Moreover, the study reported the suitability of hydrochars from BSG for soil-improvement applications [52]. Olszewski et al. [53] performed Py-GC-MS analysis BSG and corresponding hydrochars. A significant amount of N-compounds was detected at low pyrolysis temperature for spent grains, owing to weakly bonded proteins [53]. Whereas, hydrochars were characterized by fewer N-compounds released during pyrolysis, in comparison to BSG [53]. This was attributed to the Maillard reaction occurring during hydrothermal carbonization, leading to more stable N-heterocycles structures [53]. Moreover, comparison between single-step pyrolysis process and two-step process, consisting of HTC and pyrolysis, has been made by Olszewski et al. for BSG [54]. The study reported removal efficiency of inorganics for HTC temperatures between 180 °C and 260 °C, ranging from almost 60% to more than 95% for K, approx. 45% to approx. 55% for P, and approx. 35% up to approx. 75% for Na [54]. Furthermore, the study reported increased BET surface for pyrochars from two-step process, with HTC performed at 180 °C and 220 °C and pyrolysis at 600 °C, in comparison to single step pyrolysis at the same temperature [54].

Currently published studies are focused on the carbonization process of the spent grain. However, none of the published works gives an indication, if grain used for brewing, as well as the parameters of the brewing process, have any influence on the HTC process as well as on the characteristics of the spent grain and corresponding hydrochars. The aim of this research is to determine if the brewing process has any effect on the fuel parameters of spent grain and hydrochars and their respective suitability as feedstock for biorefineries. Moreover, the study also aims at a comparison between the use of direct and two different indirect methods for assessment of the performance of the HTC process in the valorisation of spent grain for energy purposes.

2. Materials and Methods

2.1. Characterisation of the Main Product–Beer

The samples of the main product, i.e., beer made in were analysed using various analytical techniques. The alcohol content was measured using Shimadzu 2010 gas chromatograph equipped with an FID detector. Injector temperature was set to 140 °C, detector to 200 °C. The split ratio was set at 30:1. Analysis was performed on ZB-WAXplus column (L = 30 m × I.D. = 0.25 mm × df = 0.25 m). Temperature program was set from 35 °C for 5 min, then raised to 85 °C (at 10 °C /min) and in the next step raised up to 200 °C (at 25 °C /min). The procedure ended with a hold period at 200 °C for 1 min. Beer extract was measured using Funke Gerber Fermento Flash beer analyser. Results are given in Brix degrees, 1 °Bx is equal to 1 g of sucrose in 100 g of solution.

An Agilent 7820 gas chromatograph coupled to an Agilent 5977B MSD Electron ionization mass spectrometer was used to determine the content of organic compounds, other than ethanol and water, present in beers. Samples of 0.5 μl were introduced into the GC injector (200 °C; split = 2); helium was used as a mobile phase (2.0 mL/min). The gas chromatograph was equipped with Stabilwax-DA column (30 m × 0.32 mm × 0.25 μm; Restek). The temperature program was set to holding at 50 °C for 5 min at first, following with subsequent temperature increase, with heating rate of 10 °C/min, up to 200 °C and holding period of 5 min. NIST-14 MS library was used for automatic identification of detected compounds by comparing mass spectra with the library's content. Only compounds with minimum match factor of 90%, in comparison to NIST library, were taken into account. The MS scanning range was m/z 10-450 with the frequency of 1.7 scan/sec. The gain factor and EM Volts

were 3.0 and 1708, respectively. The MS source temperature was 230 °C, whereas the quadrupole temperature was 150 °C. Additionally to barley and wheat-based beers, GC-MS analysis was performed for a commercially available beer, namely Primátor Weizen, brewed in the Czech Republic.

2.2. Characterisation of By-Product–Spent Grain before and after Carbonisation

Both raw and HTC treated spent grain were a subject of thermogravimetric analysis and differential thermogravimetry (TGA/DTG) analysis. The TGA/DT Pyris Diamond, manufactured by Perkin Elmer, was used. Analysis was performed according to a two-step program. Firstly, the sample was heated in up to 105 °C (heating rate of 10 °C/min), followed by a hold period of 20 min. During the second step, the sample was heated up to 900 °C with a heating rate of 10 °C/min. The nitrogen of 99.999% purity was used as inert gas. Fine particles, of particle size smaller than 200 μm, were used.

Ash content was determined using a gravimetric procedure, as described in EN 18122 [55], for combustion in a furnace at the temperature of 550 °C, using porcelain dishes. Volatile content was determined using a gravimetric procedure, as described in EN 15148 [56]. Samples in closed corundum crucibles were kept in the furnace, heated up to 900 °C, for the time of 7 min. The Perkin Elmer 2400 analyzer was used for the ultimate analysis, which was performed in compliance with the procedure set in the standard EN ISO 16948 [57]. Friedl formula [58] was used to estimate the HHV of both digestates and corresponding hydrochars:

$$HHV = 3.55 \cdot C^2 - 232 \cdot C - 2230 \cdot H + 51.2 \cdot C \cdot H + 131 \cdot N + 20600, \text{ kJ/kg} \tag{1}$$

where C, H, N represent carbon, hydrogen and nitrogen, respectively, in dry biomass (i.e., values of C, H and N are substituted, without % sign, using values from the ultimate analysis). The result of the calculation gives HHV with kJ/kg unit. Coefficients have been rounded to three significant digits. This formula was chosen, due to the fact among different types of biomass cereals were also included, which is a material relatively close, from the morphology point of view to spent grain. Friedl et al. reported a standard error of calibration of 337 kJ/kg and an R^2 coefficient of 0.943 achieved during validation of the formula (1) against the experimental results [58].

Grindability of the dried feedstocks and respective hydrochars was determined by grinding in Retsch SM100 knife mill. A screen with an aperture of 200 μm was used in the mill. Batches of approximately 200 mL of dried material were fed into the mill every 5 min until all dry material of particular HTC test was fed into the mill. For the case of both feedstocks, 400 g of dried material was used for grinding. Each of the materials, after comminutions, was a subject of sieving. A set of sieves with apertures of 1000, 800, 630, 500, 400, 300, 200, 100 and 50 μm was used in a sieve shaker to perform the particle size analysis. Sieving was performed for 30 min for each of the tests. Balance with the measurement uncertainty of 0.1 g was used for each test to check the total mass of particles, left on each sieve and the bottom pan.

2.3. Beer Brewing–Experimental Procedure and Description of the Experimental Setup

Both beers were produced in a pilot-scale brewing installation, similar to a typical, small restaurant located, craft brewery, located at the Wrocław University of Science and Technology. This installation allows producing approximately 1 hl of beer per batch, with full control over each individual unit operation of the process (Figure 1). The installation uses electricity for simplicity and convenience. However, the process heat and cold necessary for some unit operations of the brewing process (Figure 1) can potentially be delivered by other means, from other sources.
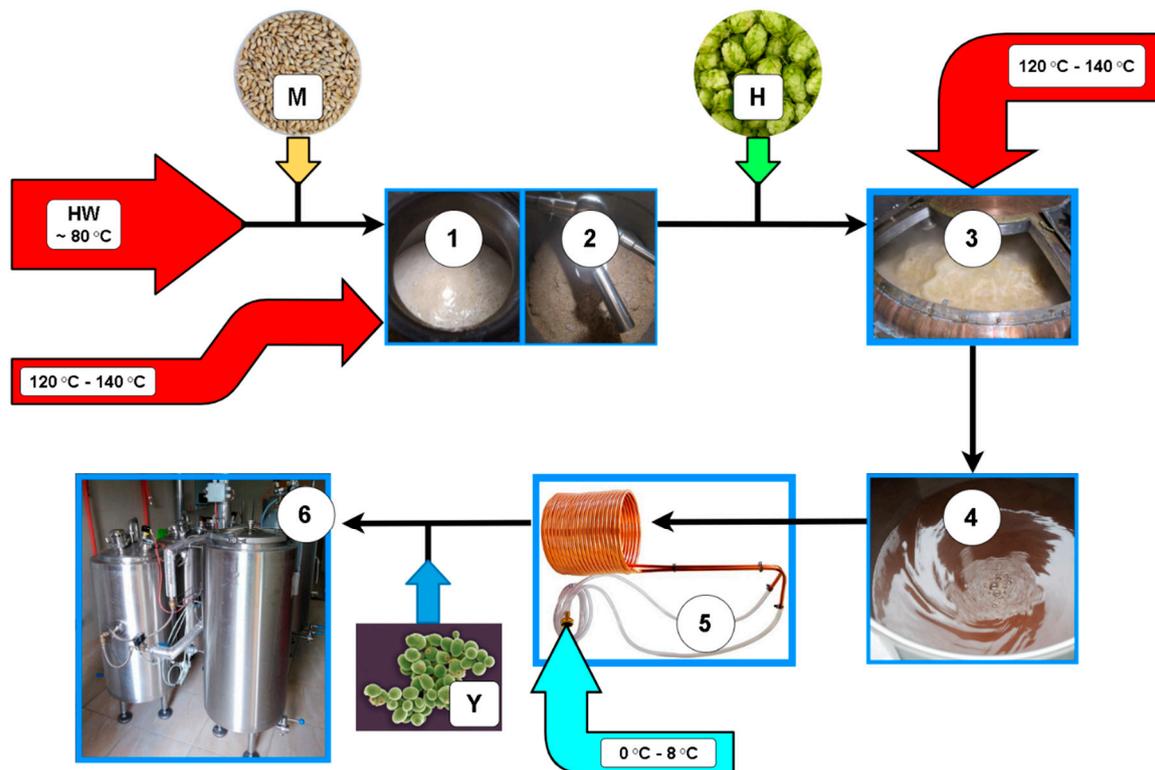
Figure 1. Pilot-scale installation diagram, with special emphasis on unit operations with heat/cold demand. Heat supply marked with red arrows, cold supply marked with a cyan arrow (1–mashing; 2–lautering; 3–boiling; 4–wort separation in a whirlpool; 5–wort cooling; 6–fermentation; M–malt; H–hops; Y - yeasts).

Beer recipes were prepared to represent two styles, distinctly different from one another and in the same time most commonly available on the market, i.e., barley beer and wheat beer. Barley-based beer was produced using, previously ground, 28 kg of pilsner malt with 70 L of water. Mashing regime was 48 °C for 15 min, 63 °C for 20 min and 73 °C for 23 min. Mashing was ended with temperature rise to 78 °C in order to kill remained enzymes. After separating sugar solution from spent grains (152 g of juniper was used as a filtration aid), 33 L of water were used for sparging remaining grains. The wort was boiled for 60 min. At the beginning of boiling 150 g of Marynka hop was added. The next dose of hops–180 g of Marynka was added 15 min before the end of boiling. Finally, the wort was cooled down to 10 °C, and 45 g of dried lager yeasts were added. Wort gravity was 17.78 Brix. Fermentation lasted for 2 weeks at 12 °C. Finally, yeasts were removed, and beer was conditioned in 5 °C for another 2 weeks.

Wheat-based beer was produced, using 4.2 kg of pilsner malt, 4.2 kg of wheat malt and 0.4 kg of caramel malt. Before mashing, grains were ground and mixed with 40 L of water. Mashing regime started at 44 °C for 20 min. Then the temperature was raised to 63 °C, and a hold period of 45 min was applied. Finally, the temperature step was 73 °C for 20 min. Mashing was ended with a temperature rise to 78 °C. After separating sugar solution from spent grains, approximately 12 L of water were used for sparging remained grains. Achieved wort was boiled for 60 min. At the beginning of boiling 30 g of Hallertau hop was added, next dose of hops–30 g of Marynka was added 15 min before the end of boiling. Finally, the wort was cooled down to 20 °C, and 22 g of dried WB-06 yeast was added. Wort gravity was 8.2 Brix. Fermentation lasted for 1 week at 23 °C. Finally, yeasts were removed, and beer was conditioned in 7 °C for another 1 week.

2.4. Hydrothermal Carbonisation–Experimental Rig and Characterisation of the Process

HTC was performed, using an autoclave (Figure 2) with a working volume of 4000 ml, able to withstand a temperature of 200 °C and pressure of 150 bar. The autoclave is equipped with a stirrer (Figure 2). However, it was not utilized during the experiments. For each experiment, approximately 400 g of dried spent grain was put into empty autoclave vessel and subsequently filled with water, up to the marking point, above which a freeboard of 500 ml remained. After sealing of the autoclave, the autoclave vessel was heated up by a heating mantle, with band heaters. K type thermocouple, connected to a PLC controller, was used in order to measure and control the process temperature. Products were drained, after cooling down of the installation, using a clean colander and a clean fabric filter. Drained material was subsequently dried. Process parameters of all performed hydrothermal carbonization experiments are given in an experimental matrix, presented in Table 1.
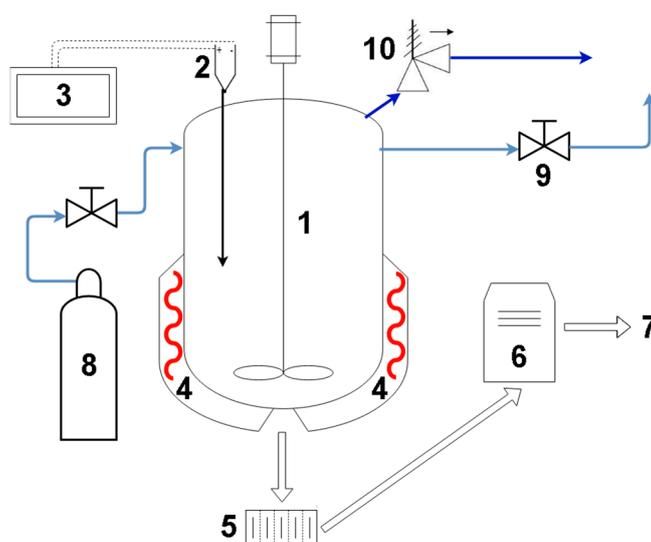
Figure 2. Diagram of the experimental hydrothermal carbonization (HTC) rig (1–Autoclave; 2–type K thermocouple; 3–PLC controller; 4–heating mantle, with band heaters; 5–draining; 6–dryer; 7–analysis of dry sample; 8–nitrogen for purging; 9–purging valve; 10–pressure relief valve).

Table 1. Experimental matrix for the suite of hydrothermal carbonization experiments.

Sample	HTC Temperature °C	Residence Time min	Average Heating Rate [1] °C / min
Barley-raw spent grain	-	-	-
Barley, 180 °C, 10 min	180	10	3.7
Barley, 200 °C, 10 min	200	10	2.9
Barley, 200 °C, 60 min	200	60	3.1
Wheat-raw spent grain	-	-	-
Wheat, 200 °C, 10 min	200	10	2.7
Wheat, 200 °C, 60 min	200	60	2.1
Wheat, 200 °C, 120 min	200	120	2.4

[1] Average heating rate, during respective HTC experiments.

Process parameters given in Table 1 were selected, based on previous works on HTC of spent grain [8,9]. It was considered by the authors, that for commercial-scale processes temperature would be minimized, as HTC process is performed under relatively high pressures, which is determined by the saturation temperature of the water, which keeps the majority of water liquid. According to Arauzo et al., 180 °C is enough to degrade polycarbohydrates [9]. Therefore, the study focused on the lower range of temperatures, typical for HTC process [27]. The residence time was deemed to

be potentially important for commercial-scale installations, as it determines the productivity for the installation of a given size. This seems to be in good agreement with reported parameters used by commercial HTC reactors for HTC of sewage sludge [59].

Mass yield (Y_m) and energy yield (Y_e) were used for assessment of performance and productivity, as typically used indicators [49,60–62]. Weber method was used, as one of the indirect methods of assessment of mass yield [49]:

$$Y_{m\ Weber} = \frac{1 - VM_{feedstock}}{1 - VM_{product}} \tag{2}$$

where: Ym–mass yield (further part of the subscript indicating a method); VM–respective volatile matter content of feedstock and product, %$_{dry}$

Moreover, the mass yield was also assessed, using well-established ash tracer method, used for indirect assessment of mass losses, during various thermal conversion processes [63]:

$$Y_{m\ ash\ tracer} = \frac{A_{feedstock}}{A_{product}} \tag{3}$$

where: Ym–mass yield (further part of the subscript indicating a method); A–respective ash content of feedstock and product, dry basis, %$_{db}$

A well-established formula was used for calculation of the energy yield [61,64,65]:

$$Y_e = Y_m \cdot \frac{HHV_{product}}{HHV_{feedstock}} \tag{4}$$

where: Y_e–energy yield; HHV–respective higher heating value of feedstock and product, MJ/kg

Ash yield was used, as suggested by Wnukowski et al. [39] and Mościcki et al. [27], as a typical indicator of the inorganic's behaviour during HTC process:

$$Y_a = Y_m \cdot \frac{A_{product}}{A_{feedstock}} \tag{5}$$

where: Y_a–ash yield

3. Results and Discussions

Overall, it could be reasonably stated that the differences in the feedstock and the brewing process resulted in two distinctly different beers. The barley-based beer had 7.6% alcohol by volume and the extract of 3.2 Brix, whereas the wheat-based beer had 3.8% alcohol by volume and extract of 1.7 Brix. GC-MS results (Table 2) show that produced beers exhibited significant differences in terms of detected aroma compounds. It could be attributed to the various malt composition in both beers and mostly thanks to differences in yeasts used for production. Moreover, it should not be overlooked that higher and richer content of aroma compounds could be found in experimental beers, in comparison to the one produced with the industrial brewing process. This may be a result of the standardization of procedures used by industrial breweries. What is more, beers brewed in the same style may have significant differences in their aroma profile or even lack in some compounds in comparison to others [66]. Thus, it seems reasonable to also expect some differences between respective by-products.

Results of proximate analysis (Figure 3) showed that in terms of fuel properties, both types of spent grain were similar. As expected, hydrothermal carbonization resulted in a decrease of volatile matter content, for both feedstocks. This is in good qualitative agreement with literature results for many different types of biomass [40,43,67,68].

Table 2. Results of GC-MS analysis of main products (beers). Values of peaks excluding water and ethanol. All compounds with match factor ≥ 90%, detected by NIST-14 MS library, presented and separated using "/". Order accordingly to respective match factors.

Compound	Barley-Based Beer	Wheat-Based Beer	Primátor Weizen
	a.u. [1]	a.u. [1]	a.u. [1]
1-Butanol, 3-methyl- / 1-Pentanol	781,362	3,160,527	n.d. [2]
2-Propanone, 1-hydroxy	245,906	202,954	274,030
Acetic acid / Ammonium acetate	3,154,572	2,101,582	802,539
2,3-Butanediol / 2,3-Butanediol, [R-(R*,R*)]- / 2,3-Butanediol, [S-(R*,R*)] [3]	4,012,472	643,145	3,721,274
2,3-Butanediol / 2,3-Butanediol, [R-(R*,R*)]- / 2,3-Butanediol, [S-(R*,R*)] [3]	2,008,409	493,655	1,512,920
2-Furanmethanol / 3-Furanmethanol / Methylenecyclopropanecarboxylic acid	2,432,529	322,155	1,307,080
Phenylethyl Alcohol / Hydrazine, (phenylmethyl)-	2,763,552	6,186,847	3,200,241
Maltol	2,689,918	591,574	4,307,609
(S)-(+)-2′,3′-Dideoxyribonolactone / 5-Hydroxymethyldihydrofuran-2-one	650,481	92,640	n.d.
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	208,087	n.d.	92,069
Glycerin	29,365,286	31,641,608	30,998,826
(S)-(+)-2′,3′-Dideoxyribonolactone / 5-Hydroxymethyldihydrofuran-2-one	40,841	85,481	n.d.
5-Hydroxymethylfurfural	470,982	n.d.	n.d.
2(3H)-Furanone, dihydro-4-hydroxy-	240,062	n.d.	n.d.

[1] a.u.–arbitrary unit; [2] n.d.–not detected; [3] two peaks detected, belonging to butanediol or one of its isomers (order of the match factors of respective compounds exactly the same for both cases).
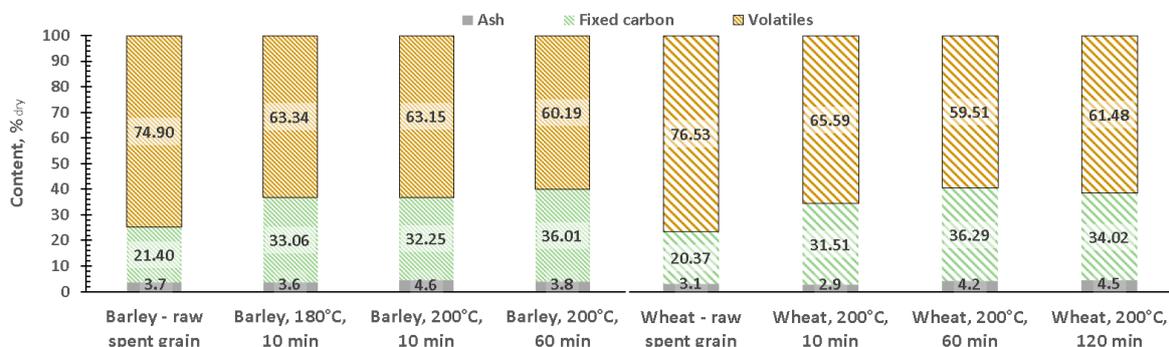
Figure 3. Results of the proximate analysis of all carbonized samples and dried feedstocks.

Increased higher heating values of hydrochars were obtained, in comparison to corresponding feedstocks (Figure 4). This is a direct consequence of the results of the ultimate analysis, as HHV was calculated for each sample, using Friedl formula (1). Nonetheless, the results obtained with this formula should be regarded as accurate for several reasons. Firstly, the standard error of calibration of 337 kJ/kg and an R^2 coefficient of 0.943 achieved during validation of the against the experimental results [58,69]. Secondly, cereals were used among the materials, used for the validation formula. As grains of various types of cereals are feedstock materials for malts, this could be considered as a material relatively close to the spent grain. Finally, the increase in HHV of material, after hydrothermal carbonization, is generally accepted trend, confirmed for various different types of feedstocks [67,70].

As could be reasonably expected from HTC process, carbonization resulted in increased C content and decreased O content, which is rather typical for this process [47,71,72]. In general, significant decrease in the oxygen content and O/C ratio (Figure 5) suggests that HTC could be a suitable pretreatment if the spent grain was meant to be used as a biorefinery feedstock, as available literature

considers high oxygen content detrimental for the quality and stability of the pyrolysis oil, attributed to the oxygenated compounds [73–75].
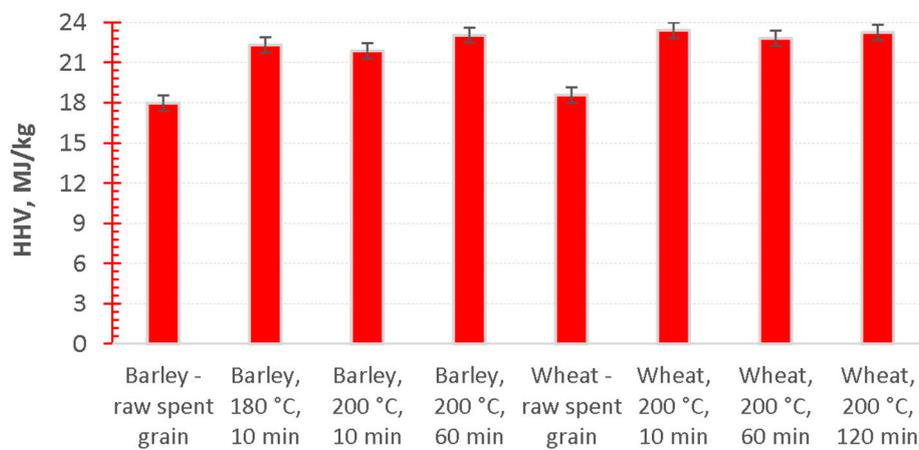

Figure 4. Higher heating value of feedstocks and respective hydrochars.
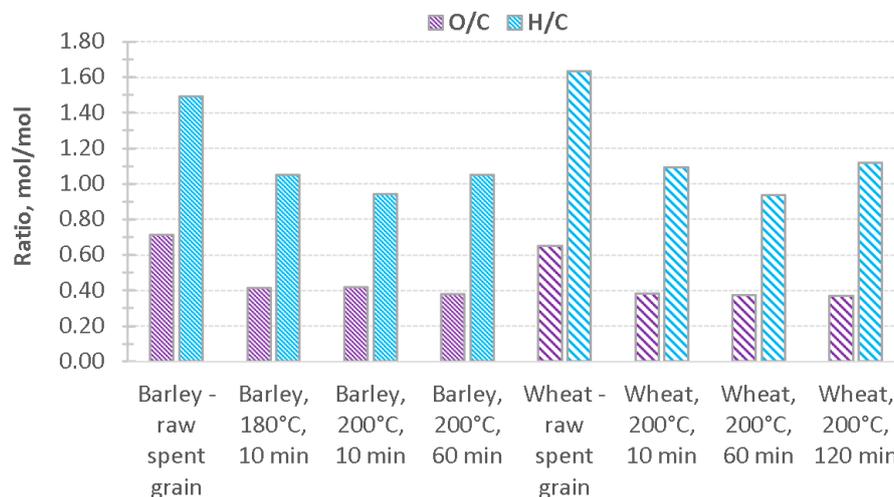

Figure 5. Molar ratios (O/C and H/C) for feedstocks and respective hydrochars.

One difference between the two feedstocks that can be clearly observed is the nitrogen content (Figure 6), which was 3.96% $_{daf}$ for barley and 6.86% $_{daf}$ for wheat BSG. Relatively higher nitrogen content of wheat spent grain could be attributed to relatively higher protein content in wheat [76,77].
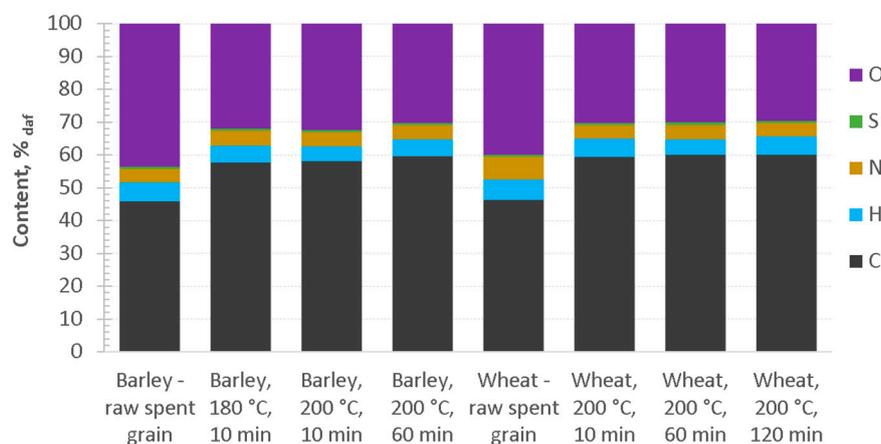

Figure 6. Ultimate analysis results for feedstocks and respective hydrochars.

Nonetheless, it should not be overlooked that nitrogen content of hydrochars was fairly similar, for both types of feedstock. Therefore, it seems sensible to hypothesize that part of nitrogen was removed due to thermal degradation of proteins during the HTC process. This decrease of nitrogen content seems to be beneficial, from the fuel perspective, as N contained in fuels tends to be a significant contributor to NO_x emissions during combustion.

Overall, it can be stated that the results of the proximate and ultimate analysis presented in other studies, published so far on HTC of BSG, support observations presented in this study [8,9,52]. Moreover, results indicate that HTC can be an important step in obtaining stable quality of solid fuels, by making them more uniform, despite the variability of the feedstock.

Overall, the indirect method for determination of the mass yield, developed by Weber et al. [49], could give satisfactory results for most of the cases (Figure 7). Only in the case of HTC of spent grain from wheat-based beer, performed at 200 °C for 120 min, the difference between the mass yield, determined by the direct and indirect method, was significant. On the other hand, the use of ash tracer method leads to significant overestimations of the mass yields, in all of the cases (Figure 7). For the results obtained by Weber method, it seems plausible to suspect that the difference was caused by the fact that inorganic content was affected to the greatest extent by the HTC process, performed at relatively long residence time. Both ash tracer method and Weber method, are based on the assumption that all of the ash, originally present in valorized biomass, remains in the solid product [49,63]. However, the Weber method compares the content of ash and fixed carbon combined, thus making the influence of any loss of inorganic part from solid fraction smaller [49]. If Y_m, determined by ash tracer method (5), is used with respective ash contents of feedstock and product to calculate the Y_a (7), then the value of 1.0 is obtained in all of the cases (Figure 8), according to the assumption made for inorganics. However, ash yields obtained, using mass yields determined by the direct method, are smaller than 1.0 in each of the cases. This indicates that a part of inorganic fraction of the original spent grain is lost. This is well in line with generally accepted consensus for hydrothermal carbonization and has been confirmed by a multitude of results from different studies, performed with different types of biomass [27,31,78,79]. Most certainly it is the case of HTC of BSG, even though a part of inorganic substance susceptible to precipitation into liquids is washed out from the malt, during the brewing process, which can be confirmed by a high content of macronutrients in various beers [80]. Poerschmann et al. [52] performed ash analysis of BSG from Reudnitzer Brewery (Leipzig, Germany) and hydrochars produced at 200 °C and 240 °C. Recovery of ash was ranging between 70% and 75% of the original mass of inorganics [52], and in case of K, only 12% to 14% remained in the solid product [52]. Poerschmann et al. [52] reported mass yields for HTC of BSG, ranging between 0.511 and 0.475, at temperatures between 200 °C and 240 °C, with the residence time of 14 h.

Arauzo et al. [9] reported mass yields for HTC of BSG from Hoepfner Brewery (Karlsruhe, Germany), ranging between 0.680 and 0. 506, at temperatures between 180 °C and 220 °C, with residence time between 2 and 4 h. The same study reported energy yields ranging between 0.835 and 0.660 [9]. This is reasonably close to the values obtained in this study for residence times of 1 and 2 h (Figure 9). The differences could be attributed to the source of the origin of BSG and the fact that this study used results of the ultimate analysis to estimate respective HHV values.
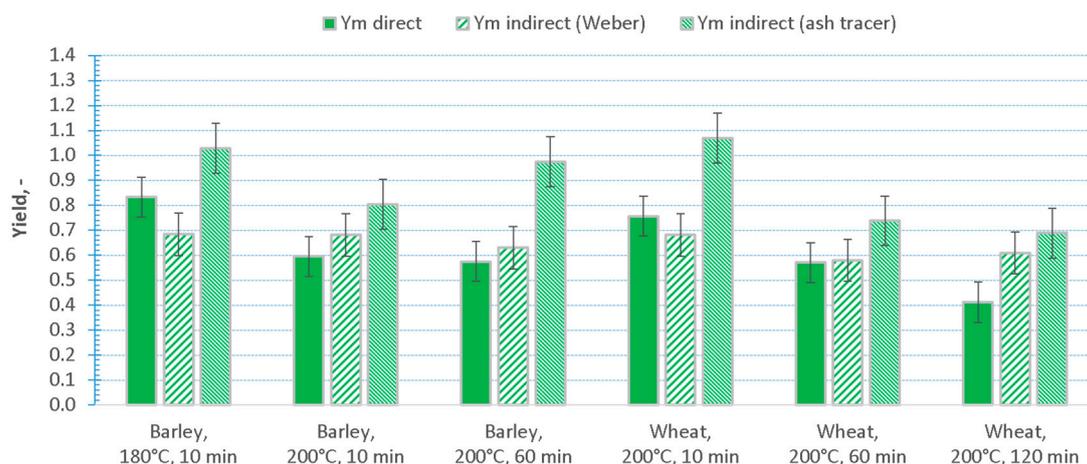
Figure 7. Comparison of mass yield, determined for hydrothermal carbonization experiments, by direct and indirect method.
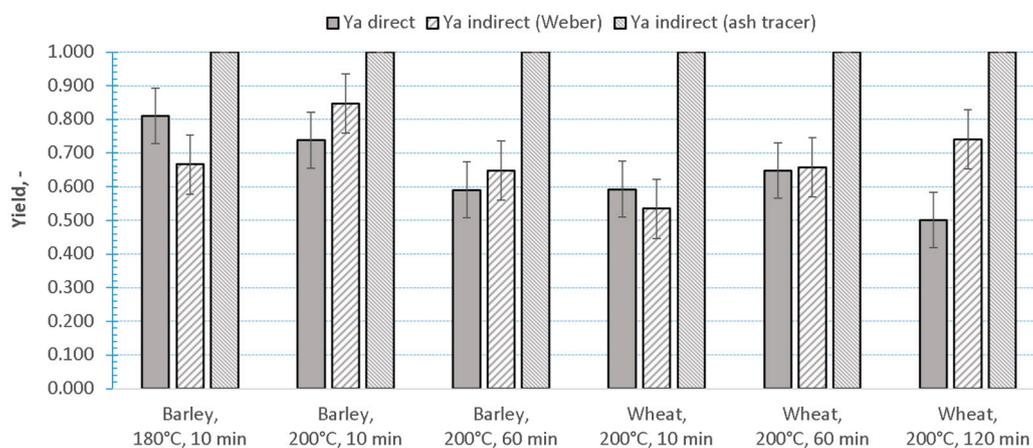

Figure 8. Comparison of ash yield, determined for hydrothermal carbonization experiments, by direct and indirect method.
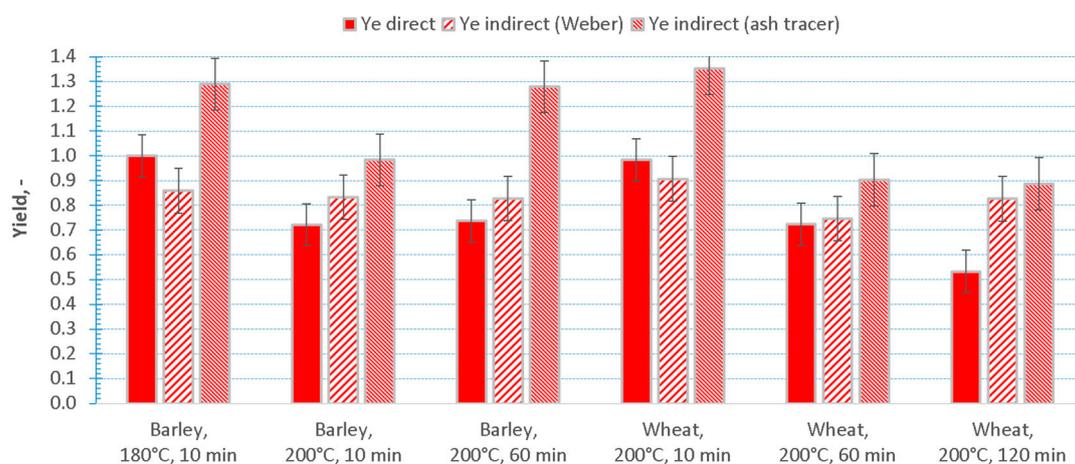

Figure 9. Comparison of energy yield, determined for hydrothermal carbonization experiments, by direct and indirect method.

More stark differences, between feedstocks and corresponding hydrochars were revealed by TGA (Figure 10) and DTG (Figure 11) analysis for pyrolysis of the samples of BSG and corresponding

hydrochars. Significant differences could be observed between DTG graphs of raw BSG samples and their hydrothermally carbonized counterparts (Figure 11). For both of the cases, raw spent grain has two distinctly different DTG peaks, one at approximately 280 °C and another close to 340 °C (Figure 11). Spent grain from wheat beer also has a small peak at approx. 225 °C, whereas for raw barley BSG this peak is minuscule and can be hardly distinguished from the adjacent shoulder (Figure 11).
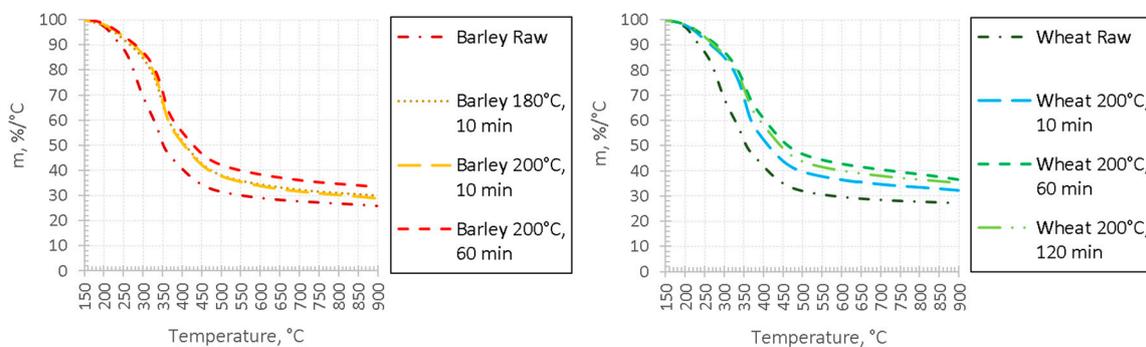
Figure 10. Results of TGA analysis of spent grains from Barley (**left**) and Wheat (**right**) and their respective hydrochars, produced in different HTC conditions (pyrolysis conditions–N$_2$).
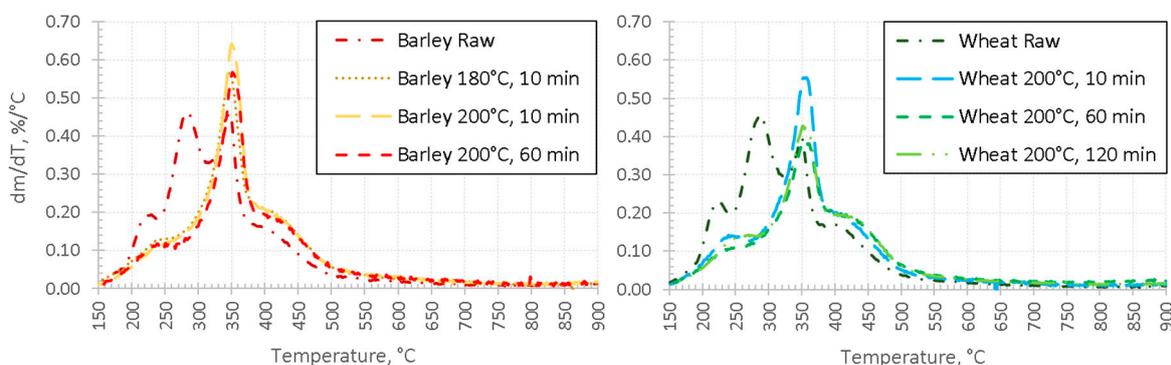

Figure 11. Results of DTG analysis of spent grains from Barley (**left**) and Wheat (**right**) and their respective hydrochars, produced in different HTC conditions (pyrolysis conditions–N$_2$).

The peaks appearing at 280 °C and 340 °C are located fairly similar to peaks that could be found in the work of Beidaghy Dizaji et al. [81] for sugar and wheat flour respectively. Therefore, it seems to be plausible to hypothesize, for both types of raw BSG, that existence of the peaks at approx. 225 °C and 280 °C was caused mainly by remaining carbohydrates, that were not processed by the yeast and decomposition of hemicellulose. Arauzo et al. [9] also attributed the large peak, present at 287 °C for pyrolysis of raw BSG and absent for pyrolysis of corresponding hydrochars, to the decomposition of the hemicellulose [9]. Similar findings were reported by Olszewski et al. [82], and the peak found exclusively for the raw spent grain at 293 °C was also attributed to hemicellulose [82]. The peak that is common for pyrolysis of raw spent grain and hydrochars, located approximately at 350 °C, was explained by decomposition of cellulose [9,82]. A similar explanation could be given for the existence of the peak present for both types of raw spent grain at 340 °C. However, it seems that it could not be attributed exclusively to cellulose and the influence of the proteins should not be overlooked, as the DTG peaks of different proteins can be found in the literature within similar temperature range [83]. This could be supported by the fact that a significant amount of nitrogen still remains in hydrochars (Figure 5), which might suggest that proteins are not fully decomposed during HTC.

In general, it seems plausible to state that HTC could be a beneficial pre-treatment as far as the use of BSG in a biorefinery is considered. Obtained results (Figure 11) show that the HTC process can make BSG more uniform, as similar DTG profiles could be obtained for BSG samples from the brewing of distinctly different styles of beer. Moreover, HTC allowed maximized release of volatiles closer to

the temperature region, typical for pyrolysis, aiming at the production of liquids. In contrast to raw BSG samples with a couple of peaks present within a relatively wide range of temperatures, pyrolysis of hydrochars resulted in a single sharp peak close to 350 °C. It seems reasonable to expect that, in such cases, devolatilization would lead to more uniform products which in turn could lead to more uniform composition of pyrolysis oil, after quenching. More research is needed to confirm this hypothesis.

Particle size can have a significant influence on the pyrolysis process [70]. Kinetic data is only relevant for small enough particles, where heat transfer becomes irrelevant [84]. Therefore, additional positive effects of hydrothermal carbonization, as a pre-processing technique for biorefineries, can be clearly seen in Figures 12 and 13. In the case of both feedstocks, HTC resulted in significant improvement of the grindability of hydrochars, in comparison to the raw, dried spent grain. Not much can be found in the literature, regarding the influence of HTC on grindability. Nonetheless, the results presented in this study are in good qualitative agreement with existing literature sources. Wnukowski et al. [39] presented particle size distribution of raw and wet torrefied miscanthus, after comminution in a knife mill. Clear similarity with Figure 12 in this study could be seen as grinding of hydrochars significantly increased the share of fines in the comminuted sample. Moreover, also in the case of miscanthus the differences between respective particle size distributions of samples, carbonized in different HTC conditions, were not as significant as the difference between hydrochars and raw miscanthus [39]. However, the extent of this improvement was much greater, in comparison to this study, as only slightly more than 20% of total sample mass consisted of particles smaller than 500 µm, for a cumulative share of particles of raw miscanthus after comminution [39]. A similar trend was reported for miscanthus by Kambo and Dutta [78], with some differences in particle size distribution that could be attributed to the use of different mill (ball mill) [78]. Sharma et al. [85] also reported similar behaviour, for HTC of yard waste, with subsequent milling in a ball mill. Yard waste, collected in autumn, consisted of 65% (wet biomass) of tree leaves, 33% of grasses and garden trimmings as well as 2% fallen sticks and flowers [85]. Overall, it is not surprising that dried spent grain is more grindable in comparison to herbaceous biomass or mixture of herbaceous and woody biomass. This could be undoubtedly attributed to the fibrous nature of lignocellulosic and herbaceous biomass, which is not the case for malt.
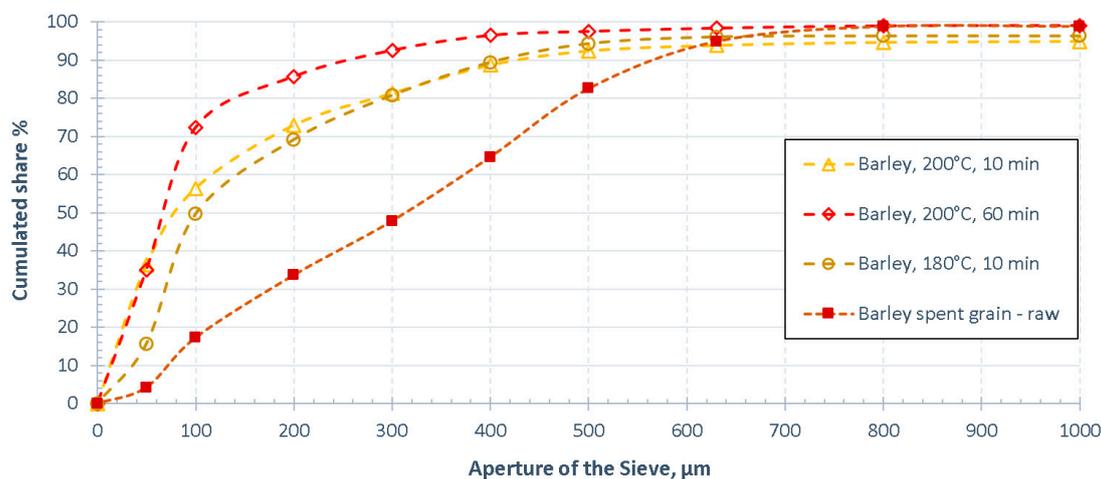
Figure 12. Particle size distribution after grinding spent grain from barley-based beer and respective hydrochars in Retsch SM100 knife mill.
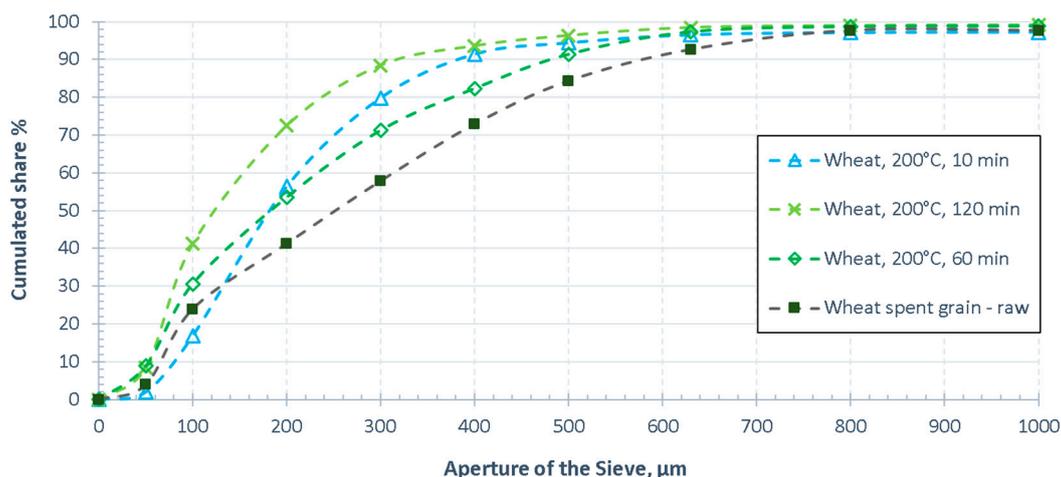
Figure 13. Particle size distribution after grinding spent grain from wheat-based beer and respective hydrochars in Retsch SM100 knife mill.

Figures 12 and 13 show particle size distribution of dried spent grains and corresponding hydrochars. It can be clearly seen that HTC process had positive influence on the grindability for both feedstocks (Figures 12 and 13). However, the extent of the improvement in the grindability, due to use of the HTC process, was different for spent grain from barley and wheat beers (Figures 12 and 13). This could be attributed to the addition of small, slashed branches of juniper, which is fibrous, lignocellulosic biomass. Moreover, malt is a subject of comminution before brewing, and during the process, malt is further broken down physically and thermally, during mashing, lautering and boiling (see Figure 1). Furthermore, the growth of the yeast during fermentation can be considered as a contribution of a part of the mass of the spent grain, at the end of the brewing process [86], which by nature is not hard and durable, thus easy to grind. It could be sensible to recommend further research on the influence of this friable nature on the pelletizing behaviour, as some studies have already reported relatively easy pelletizing of hydrochars [29,87]. According to some of the published studies, it is possible to decrease the energy requirement for pelletizing decreased by half and three quarters, in comparison to typical wood pellets torrefied wood pellets, respectively [88].

Detailed mass, energy and carbon balances are presented, for selected HTC conditions for both types of spent grain, in Figure 14. It is difficult to select optimum HTC conditions if pre-processed feedstock is intended to be used in a biorefinery, if quality of the pyrolysis oil cannot be assessed. Nonetheless, existing literature indicates that oxygen has detrimental influence on quality of pyrolysis oil, as it increases the content of unstable oxygenated compounds among the liquid products of pyrolysis [73,74,89]. Therefore, the lowest possible O/C content (Figure 4) was ultimately chosen as the criterium of this selection. Based on this criterium, HTC at 200 °C, with residence time of 60 min, has been selected as optimum pretreatment conditions for both types of feedstock.

A part of carbon is lost to the liquids in both of the cases presented in Figure 14. Similarly, approximately one third of the original chemical energy of the feedstock is lost to by-products. However, this energy can be recovered by adding this liquid into anaerobic digestion reactors, as suggested by many studies of HTC of different types of biomass [43,69,90–95].

It seems prudent to suggest more research in two areas. Firstly, extensive research on composition of pyrolysis oil from HTC treated BSG, including influence of the particle size, would be beneficial in terms of obtaining definite answer on optimum HTC parameters for biorefinery purposes. Moreover, anaerobic digestion of liquid by-products of HTC of brewer's spent grain should also become a subject of detailed experimental investigation.
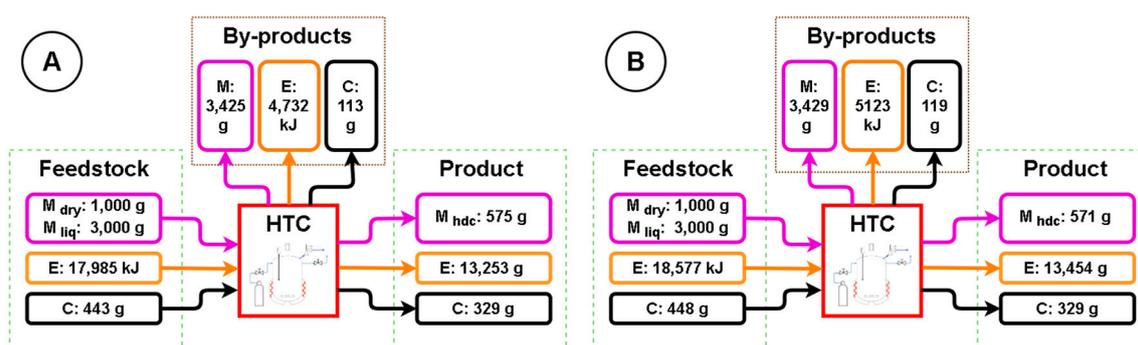
Figure 14. Mass, energy, and carbon balance for selected HTC parameters: A–Barley-based BSG after HTC at 200 °C, 60 min; B–Wheat-based BSG after HTC at 200 °C, 60 min. (M–mass; M_{dry}–mass of dry solids; M_{liq}–mass of water; M_{hdc}–mass of dry hydrochar; E–energy; C–carbon).

4. Conclusions

Overall, the differences in the feedstock and parameters of the brewing process resulted in two different beers. Thus, it was reasonable to expect two distinctly different by-products (BSG) as a result. However, the differences in terms of the fuel properties of both types of BSG were much less stark in comparison to the initial assumptions.

In general, the use of HTC as a pretreatment of BSG for subsequent use as a biorefinery feedstock can be considered beneficial. HTC was helpful in uniformization and improvement of the fuel properties. Significant decrease in the oxygen content and O/C ratio, which should be considered beneficial, as available literature considers high oxygen content detrimental for the quality and stability of the pyrolysis oil, attributed to the oxygenated compounds. The HTC process made BSG more uniform, as similar DTG profiles could be obtained for BSG samples from the brewing of distinctly different styles of beer. Moreover, HTC allowed maximized release of volatiles closer to the temperature region, typical for pyrolysis aiming at the production of liquids. In contrast to raw BSG samples with a couple of peaks present within a relatively wide range of temperatures, pyrolysis of hydrochars resulted in a single sharp peak close to 350 °C.

The extent of the improvement in the grindability, due to use of the HTC process, was different for spent grain from barley and wheat beers. However, in both of the cases, improvement of the grindability could be observed.

From the indirect methods for assessment of the productivity of the HTC process, the Weber method could give satisfactory results for most of the cases. Traditional ash tracer method resulted in significant overestimations of the mass yield, thus making this method not suitable for the future use in commercial-scale installations.

It seems to be reasonable to recommend further research on the influence of HTC on the overall quality and composition of pyrolysis oil from pyrolysis of BSG. Further research on different routes of the utilization of HTC liquid byproducts, such as the use of this liquid for anaerobic digestion, is also recommended. Filling this knowledge gap is a prerequisite for the practical implementation of the HTC process in the future biorefineries, conforming to the circular economy standards.

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