Brewer's Spent Grains

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Brewer's spent grains (BSG) is the main solid by-product in the brewing industry, obtained during lautering. BSG has a multitude of applications and it can be used as a valuable fedstock for production of different products. Moreover, it could also be used as a biomass for energy purposes.

Solid Fuel Brewer's Spent Grain Hydrothermal Carbonisation

1. Introduction

The main solid by-product in the brewing industry is brewer's spent grains (BSG) obtained during lautering [1].

Industrial-scale breweries produce high quantities of mentioned wastes and are able to deliver it constantly. According to Eurostat, 34 billion L of beer was produced in the European Union in 2019 [2]. That means that large quantities of brewer's spent grains are produced yearly. Such by-product is rich in cellulose, hemicellulose, lignin, and proteins (Table 1). It may be feasible to use them in the neighbourhood of such factories due to the high costs of transport.

Table 1. The approximate chemical composition of BSG in different studies (% of dry weight).

	Lignin	Cellulose	Hemicellulose	Ash	Protein	Lipids	Phenolics	Starch
Kanauchi et al., (2001)[3]	11.9	25.4	21.8	2.4	24.0	10.6	N.D.	N.D.
Carvalheiro et al., (2004)[4]	21.7	21.9	29.6	1.2	24.6	N.D.	N.D.	N.D.
Silva et al., (2004)[5]	16.9	25.3	41.9	4.6	N.D.	N.D.	N.D.	N.D.

Mussatto and Roberto, (2006)[6]	27.8	16.8	28.4	4.6	15.2	N.D.	N.D.	N.D.
Celus et al., (2006)[7]	N.D.	0.3	22.5	3.3	26.7	N.D.	N.D.	1
Xiros et al., (2008)[8]	11.5	12	40	3.3	14.2	13	2.0	2.7
Jay et al., (2008)[9]	20–22	31–33	N.D.	N.D.	15–17	6–8	1.0–1.5	10–12
Treimo et al., (2009)[10]	12.6 ± 0.1	45.9 *			23.4 ± 1.4	N.D.	N.D.	7.8 ± 0.2
Robertson et al., (2010)[11]	13–17	N.D.	22–29	N.D.	20–24	N.D.	N.D.	2–8
Khidzir et al., (2010)[12]	56.74 ± 9.38	40.20 ± 17.71	N.D.	2.27 ± 0.76	6.41 ± 0.31	2.50 ± 0.11	N.D.	0.28 ± 0.06
Waters et al., (2012)[13]	N.D.	26.0	22.2	1.1	22.1	N.D.	N.D.	N.D.
Meneses et al., (2013)[14]	19.40 ± 0.34	21.73 ± 1.36	19.27 ± 1.18	4.18 ± 0.03	24.69 ± 1.04	N.D.	N.D.	N.D.

Sobukola et al., (2012) [15]	9.19 ± 0.011	60.64 ± 0.26 *	2.48 ± 0.02	24.39 ± 0.46	6.18 ± 0.13	N.D.	N.D.
Kemppainen et al., (2016)[16]	19.6	45 *	4.1	20.3	N.D.	N.D.	N.D.
Yu et al., (2020)[17]	N.D.	51.0 ± 0.7 *	4.1 ± 0.1	23.4 ± 0.2	9.4 ± 0.1	N.D.	N.D.

N.D.—no data, *—all carbohydrates.

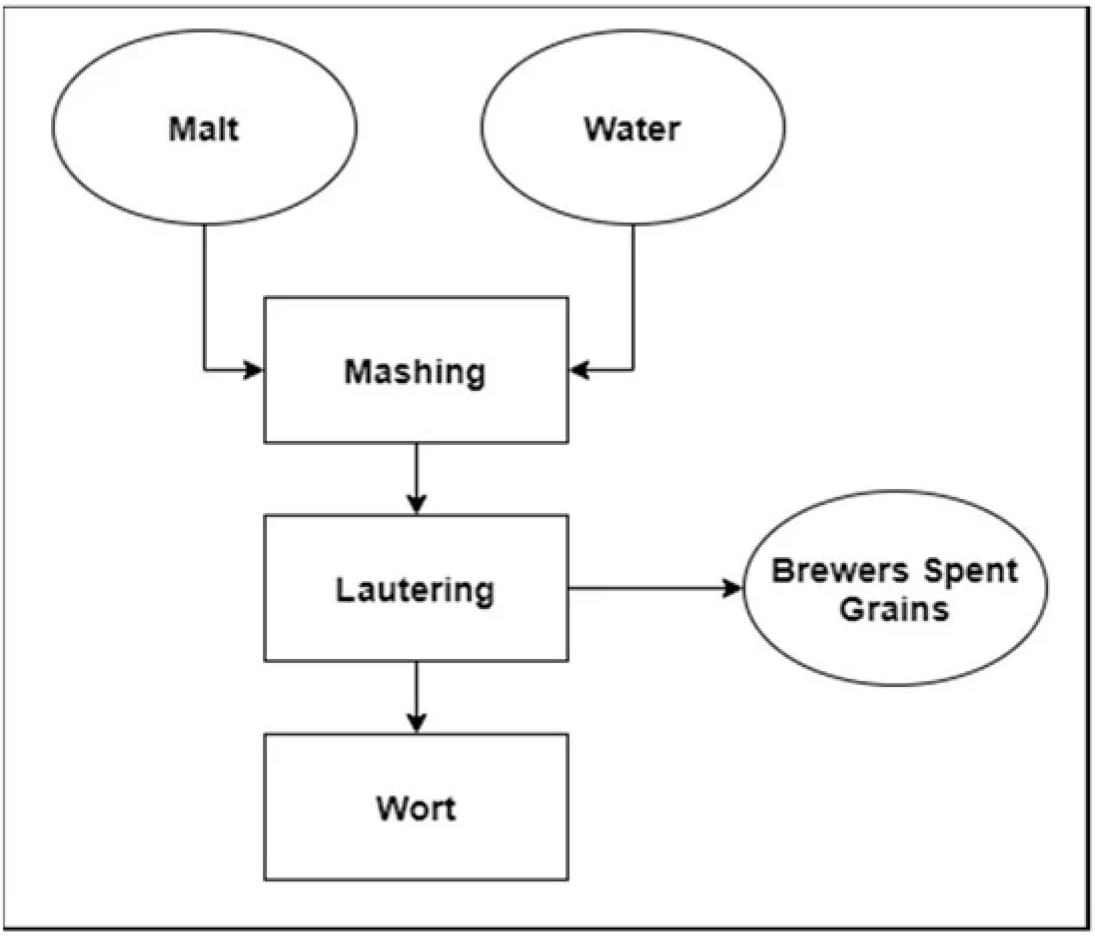

Figure 1. Diagram of beer wort production with an emphasis on the main solid by-product.

2. Thermal Valorization of BSG

2.1. BSG as a Solid Fuel

Basic fuel properties, reported by many researchers, suggest that BSG is promising as a solid fuel (Figure 2) [18][19]. Reported carbon content reported is typically ranging between 45% up to approx. 49% on the dry basis [18][19], which makes BSG not significantly different in terms of its fuel properties, in comparison to lignocellulosic biomass. Additionally, ash content varies between 2 and 6% [19][20][21], which is similar to different types of agricultural biomass [22][23][24][25][26][27][28]. However, high moisture content, exceeding 70% [18][19], is a significant obstacle in the use of BSG as a solid biofuel. Drying is possible but requires energy and bulky installations due to relatively high residence time, e.g., the order of magnitude of 100 min was reported by some studies [29] for achieving moisture reduction of 0.2 of the original value, corresponding with the moisture content of approx. 15%. Moreover, the energy required for the drying process should not be overlooked. Some studies [30] reported drying energy, for superheated steam drying of BSG, ranging between 0.65 and 1.45 MJ/kg of removed water, when latent heat recovery from steam was included in the balance [30].

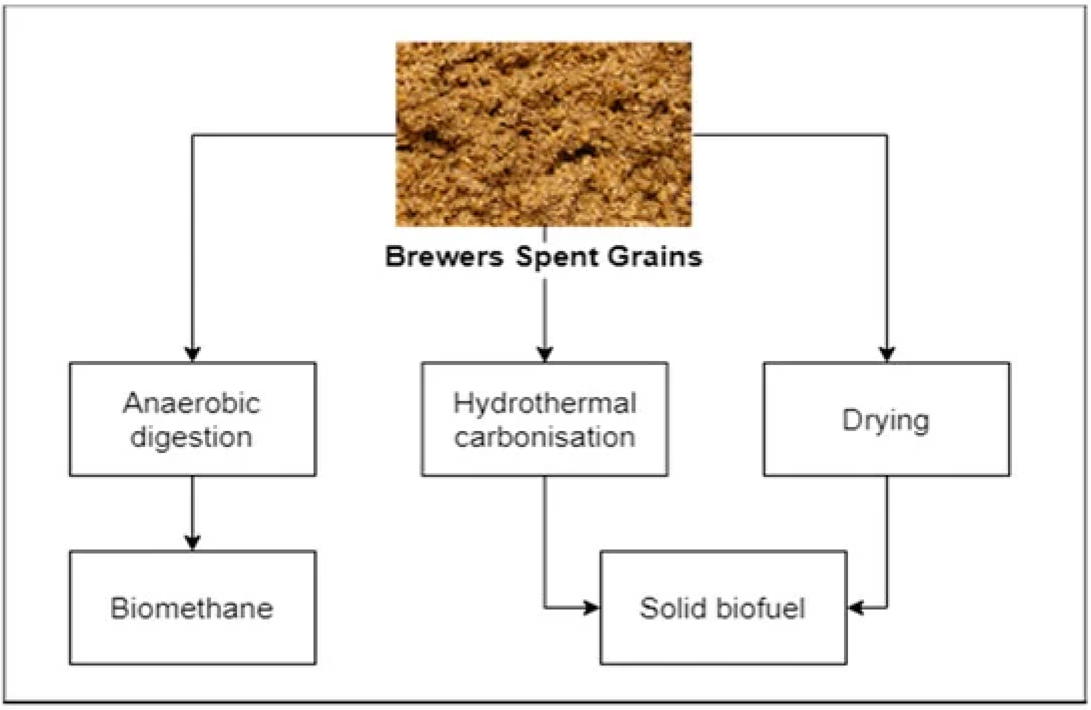

Figure 2. Energetic valorization of BSG.

2.2. Hydrothermal Carbonization as a Thermal Valorization Method for Wet Types of Biomass

HTC is a thermal valorization process, typically performed at elevated temperatures (typically 200 to 260 °C) in subcritical water, at elevated pressure [31][32]. The use of such a process can enhance mechanical dewatering, which has already been reported for various wet types of biomass [33][34][35].

The ionic constant of water is significantly increased, and water behaves as a non-polar solvent at 200–280 °C [35][36][37][38][39][40][41]. A multitude of reactions occurring at the same time, with the output of multiple different products, can be considered characteristic for HTC of complex substances such as different types of biomass [32]. The HTC process starts with hydrolysis [31]. This is followed by dehydration and decarboxylation [31][42]. Dehydration decreases the amount of hydroxyl groups (OH) [31]. The decrease in the amount of OH groups also causes a lower O/C ratio. Decarboxylation decreases the amount of carboxyl (COOH) and carbonyl (C=O) groups, also slightly decreasing the O/C ratio of the solid product [31]. This is followed by polymerization and aromatization [31][42]. A decrease in the number of hydroxyl groups is the key aspect in making hydrothermally carbonized biomass more hydrophobic, lowering its equilibrium moisture content [43] and making physical dewatering easier [31]. The ability to decrease O/C ratio is beneficial when valorization is performed, aiming at improving the results of subsequent pyrolysis [44][45][46]. Moreover, the process of hydrothermal carbonization can change the biomass in terms of the composition of the inorganic fraction [32][47]. Furthermore, some studies reported relatively easy pelletizing of hydrochars [48]. This makes hydrothermal carbonization a prospective valorization process for low-quality solid biofuels, especially when wet biomass is concerned as a potential feedstock.

2.3. The Effect of Hydrothermal Carbonization of BSG

Slight improvement in mechanical dewatering, thanks to HTC of BSG, was observed [34]. Moreover, the GC-MS analysis of the liquid HTC effluent indicated that it contains organic compounds that could be used to produce biogas in the anaerobic digestion [34]. Similarly, phenols, benzenediols, and fatty acids can be found in the liquid by-products of HTC of BSG, concluding that the release of such compounds is an effect of the presence of bound lipids in the feedstock [49]. HTC of spent grain from a big scale brewery, resulted in an improvement in fuel properties. Higher heating value (HHV) increased, accompanied by a decrease in the ash content, especially for high water: biomass ratios [50]. The study deemed low temperatures of the HTC process especially suitable, thanks to the high content of hemicellulose in the feedstock [50]. For HTC of BSG the mass yield can be determined by an indirect method [51]. Moreover, it has been confirmed that HTC can increase the heating value of BSG and decrease the O/C ratio [51], indicating its suitability as a valorization method suitable for subsequent pyrolysis.

A Py-GC-MS analysis of BSG and corresponding hydrochars were performed. It was noticed that relatively low pyrolysis temperature for spent grains resulted in a release of a significant amount of *N*-compounds, which was attributed to weakly bonded proteins present in the feedstock [52]. On the other hand, fewer *N*-compounds was released during pyrolysis of hydrochars, owing to the Maillard reactions producing more stable *N*-heterocyclic structures [52]. Hydrothermal carbonization, performed at temperatures between 180 and 260 °C, resulted in the removal efficiency of inorganics, 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 [53]. Moreover, HTC performed at 180 and 220 °C, and pyrolysis at 600 °C resulted in increased BET surface for pyrochars from a two-step process, when comparing to single-step pyrolysis at the same temperature [53].

3. Extraction of High-Value Compounds from BSG

Due to the multitude of compounds contained, the brewer's spent grain undergoes extraction processes to obtain substances with the desired properties. BSG undergoes many different extraction processes, such as alkaline hydrolysis [54], enzymatic hydrolysis [55],microwave-assisted extraction [56], solvent extraction[14], supercritical carbon dioxide extraction [57], ultrasound-assisted extraction [58], etc. The products that can be obtained by extraction are:

3.1. Arabinoxylans, Polyphenol, Antioxidants and Glucose

Arabinoxylan is a polysaccharide consisting of two pentose sugars: xylose and arabinose [59]. Among other hemicelluloses, cellulose, and lignin, it is part of the dietary fibre found in BSG. It can bind to polyphenols such as ferulic acid and *p*-cumaic acid. Arabinoxylans can be recovered by ultrasound-assisted extraction [58], microwave-assisted extraction[56] or HCl and ethanol extraction (after previous protein extraction) [60].

Studies show that supercritical extraction of CO_2 with ethanol 60% *v/v* at 35 MPa, 40 °C at an extraction time of 240 min allows a good recovery of phenolic or flavonoid fractions [57][61]. The extract obtained is characterized by good antioxidant properties. Phenolic fractions can also be obtained by solvent extraction (acetone–water mixture) [14]. Good recovery of ferulic and *p*-coumaric acids is provided by the BSG alkaline extraction [54] and solvent extraction (acetone: water mixture) [14][62]. For ultrasound-assisted extraction of polyphenol compounds from BSG, experimental data were in good agreement with both power law and the Weibull model [63]. Ultrasound-assisted extraction achieved similar productivity, after 30 min of treatment, in comparison to enzyme hydrolysis [63]. Comparison of conventional maceration, microwave and ultrasound-assisted extraction, using BSG from light and dark beer as well as their mixtures concluded that microwave and ultrasound extraction did not improve the total polyphenol yield [64]. As the result of the use of *Bacillus subtilis WX-17* to improve the nutritional value of BSG in a solid-state fermentation the total amount of unsaturated fatty acid and the total antioxidant quantity can increase by as much as 1.7 and 5.8 times, respectively[65]. Extraction of phenolic antioxidants from BSG, using acetone–water and ethanol–water mixtures as extraction solvents, achieves maximum yield at 60% (*v*/*v*) organic solvent concentration, for both solvents [66].

3.2. Proteins

Due to the high protein content (about 20% in dry matter), BSG is a good potential source of vegetable protein for the food industry. In the case of protein extraction, the selectivity of the extraction process is crucial. Alkaline treatment of BSG, resulted in the extraction yield of 21.4% and purity of 60.2% for extracted proteins [67]. In case of a combination of alkaline pretreatment with diluted acid, a very high degree of extraction was obtained (even 95%). However, the selectivity of protein extraction process has some drawbacks, because part of lignin and hydrocarbons contained in BSG can be dissolved together with proteins [68]. Good selectivity, with lower horizontal extraction (about 65%) can be obtained with hydrothermal pretreatment, which does not require the use of chemicals [68]. Good results of the extraction of proteins from BSG (up to 80%) were achieved with the use of carboxylate salt—urea DES [69]. The disadvantage of this technology is the residual DES in the protein product, but in a case when a substitute for urea will be gained, this method could be attractive for making human nutrition products. Another promising method is the use of ultrasounds for enzymatic hydrolysis of proteins from BSG [17].

By using ultrasound pretreatment, the efficiency of protein separation is increased (from 61.6 to 69.8%), the time of enzymatic reaction is shortened (by 56%), and the cost of enzyme use can be reduced (even 73%).

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