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# Valorisation of Brewer's Spent Grain: Lignocellulosic Fractionation and its Potential for Polymer and Composite Material Applications

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## Abstract:

An estimated amount of 40 million t/a of Brewer's Spent Grain (BSG) is produced and is currently used for low-value valorisation or disposed of in landfills. In an era where non-renewable resources stocks are depleting and products such as plastics accumulate in the environment, the need for more sustainable resources, products and production strategies is substantial. Lignocellulosic biomasses, when their production is not in competition with the food sector, could be an answer to this challenge through the use of biorefineries. This review aims at gathering the advantages of BSG's valorisation through the prism of building block production for polymer synthesis and its use as natural filler for composite material. BSG will also be compared to other biomasses by exploring the conditions available for its fractionation. The examples listed herein depict promising valorisation strategies with a myriad of building blocks available for the synthesis of organic compounds and polymers. The use of BSG as filler in composite materials, however, faces limitations in terms of performances that will need to be tackled in future works. A lot of research has yet to be performed on BSG's valorisation to help shift the polymer and material industry towards a more sustainable horizon.

**Keywords:** Brewer's spent grain, bio-based building blocks, biopolymer, composite materials, green chemistry, sustainability.

## 1 Introduction

In a context where our economical and consumption model is mainly designed to be linear, the global annual production of wastes is estimated around 2 billion t/a, continuously

29 growing to reach the expected amount of 3.4 billion t/a by 2050. An evolution of the  
30 consumption and production habits has recently been witnessed, supported by the scientific  
31 community through the development of green chemistry for example, providing new and  
32 greener alternatives to meet the demands of sustainable production. Plastic is one of the largest  
33 pollutants with a generation of more than 350 million t/a waste globally, according to the  
34 OECD (Organisation for Economic Cooperation and Development) with only 9-10% of  
35 material being recycled. [1] [2] Furthermore, plastics are majorly petroleum based and non-  
36 biodegradable leading to an accumulation of such materials in the environment and a  
37 dependence on non-renewable resources, highlighting the necessity for a more sustainable  
38 design for material production. To this end, the use of biomass can be appealing to meet the  
39 challenges presented. In particular, the by-products of the agri-food industry are often under-  
40 utilised or valorised for low-value products. The conception of novel polymeric materials with  
41 good biodegradability profile, low toxicity and ecotoxicity, while using wastes as raw  
42 materials, is a necessary step to drive this industry towards a more sustainable future. New  
43 synthetic and production strategies are thus required to obtain new monomers to be used as  
44 building blocks for polymers and composite materials. In this review, the focus will be placed  
45 on the valorisation of Brewer's Spent Grain (BSG), a by-product from the brewing industry, a  
46 promising under-utilised and undervalued renewable raw material. The valorisation of waste  
47 biomass as feedstock described herein is in accordance with the 12<sup>th</sup> Sustainable Development  
48 Goal listed by the Department of Economic and Social Affairs from the United Nations. [3]

#### 49 Barley and BSG

50 While the brewing activity started approximately 6000 years ago by the Sumerians [4],  
51 the global production of its major component: barley (*Hordeum vulgare L.*) reached 141 million  
52 t/a in 2016 [5] [6], corresponding to an overall estimated beer production between 182 and 340  
53 billion litres/a from 2016 to 2021 [7] [8] [9]. While the fermentable sugars (wort), extracted after  
54 mashing and sparging, will be used for beer production through fermentation, the main by-  
55 product of the brewing process is BSG (Brewer's Spent Grain). BSG represents **85% of the by-**  
56 **products** [4]; 100 kg of malt will produce 100-130 kg of BSG with a high **moisture content (MC)**  
57 **between 70-80%**. The production of BSG is commonly estimated at 20 kg/100L of beer [10] [11]  
58 [12], which represents a global production of 36.4-39 million t/a in 2019 [8] [9] [10] [11] [13]

59 [14], raising over **40 million t/a** today and corresponds to a waste generation of 3.4 million t/a  
60 (2008) in Europe alone. [15]

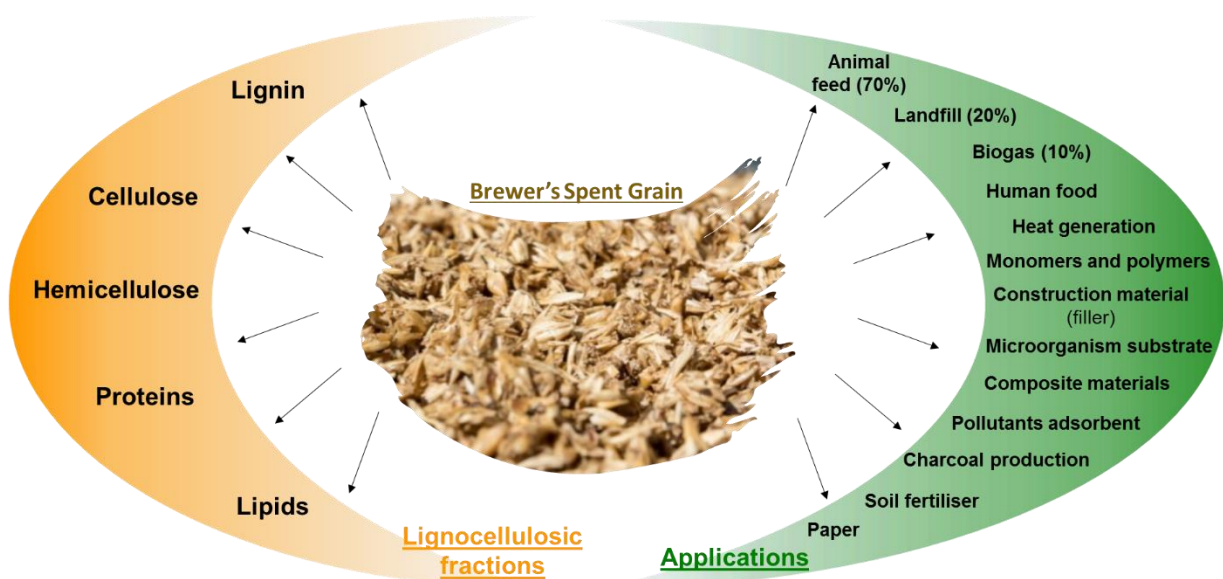
61 BSG is an inexpensive raw material with an estimated cost around 35€/t of dry matter  
62 [13] or 42 USD/t [16]. Its all-year-round availability and low cost make it an interesting resource  
63 for various applications. However, it is rapidly perishable due to microbiological instability:  
64 high MC and presence of fermentable sugars, with a shelf life of 2-10 days depending on  
65 storage conditions. [17] Due to its high moisture content, the major part of its cost is brought  
66 by the transport [18] but mainly by the drying process of this biomass [16] with a high  
67 environmental impact of 495-770 kg<sub>CO2</sub>/t<sub>BSG</sub> (CO<sub>2</sub> equivalents) for the latter. Arranz et al. have  
68 developed a solar oven as an alternative to conventional drying techniques for BSG  
69 (convection drying [19] or infra-red drying [20]), lowering the environmental impact to 0  
70 kg<sub>CO2</sub>/t<sub>BSG</sub> but increasing the drying time 10-fold. [18] The elimination of the water contained  
71 in renewable biomass is a major challenge that needs to be taken into account when designing  
72 valorisation routes to prevent having a greater environmental impact than the petroleum-  
73 based counterpart they try to supplement. Examples of biomass valorisation have shown that  
74 water elimination can cover up to 80% of the energy cost, before the actual valorisation process  
75 even begins. [21] Thus, an LCA (Life Cycle Analysis) should be performed when possible to  
76 confirm the benefit of such routes and new materials. By assessing the techno-economic  
77 feasibility, the environmental impacts and energy consumption of BSG's valorisation, a recent  
78 study showed that water removal was indeed an important step of the process in terms of  
79 environmental impact, advocating mechanical dewatering such as screw, centrifugal,  
80 hydraulic or membrane filter presses. Without eliminating the risk of microbial growth of BSG  
81 like a complete drying would, the mechanical dewatering should prolongate the shelf-life of  
82 BSG before its valorisation, that can be as low as 48 hours for wet BSG (with around 80% WC).  
83 Alternative drying methods such as microwave drying could eliminate water with a limited  
84 CO<sub>2</sub> emission, reaching moisture levels below 10%. [22]

85 Finally, the use of this massively produced bio-based waste that is BSG has attracted the  
86 scientific community's interest only recently with a few publications per year in the 80's up to  
87 around 330 annually more recently [23], still timid considering the volumes generated and the  
88 low-value valorisation to this date. In 2020, 70% of the BSG was valorised for animal feed, 10  
89 % for the production of biogas, while 20% were eliminated in landfills. [17] This last option to

90 dispose of the BSG waste equates to an **environmental impact of CO<sub>2</sub> eqv =513 kg/t<sub>BSG</sub>**. [24] It  
91 would thus be important to valorise this resource more efficiently by producing higher value  
92 products that would encourage breweries to further upcycle this resource.

93 This review aims at showcasing the advantage of BSG over other biomasses and  
94 covering the applications (Figure 1) where large volumes of BSG could be used to produce  
95 higher value products such as polymers and composite materials. This could be performed by  
96 fractionation of its lignocellulosic matrix (Figure 1), yielding various building blocks for  
97 polymer synthesis. After a meta-analysis of the composition and an overview of the of the  
98 available applications for BSG, a study of the reported works for the fractionation of its  
99 lignocellulosic matrix will be presented, with a stronger focus on monomer production. Then,  
100 the scope of building blocks obtainable from BSG will be investigated, followed by their use  
101 for polymer synthesis. The use of BSG with limited transformation as renewable filler for  
102 composite material application will be described.

103 A lot has yet to be explored in the field of polymer and material chemistry for an efficient  
104 usage of BSG, and this review will help outlining the opportunities and challenges for the  
105 valorisation of BSG through the prism of biomass fractionation for polymer and composite  
106 material applications, which were not reviewed to this date. This review will consider articles  
107 treating BSG's matrix fractionation and other biomasses for comparison and publications  
108 focusing on monomer production from BSG for polymer synthesis as well as the use of BSG  
109 for composite materials.



110

111 **Figure 1** Fractions present in BSG's lignocellulosic biomass and their potential applications.

## 112 2 Composition

113 BSG's composition varies greatly depending on various parameters such as barley  
114 variety and type (grilled, roasted, according to beer type), kilning temperature (KT, drying of  
115 the green malt after germination), malting process, mashing conditions, to name but a few. [6]  
116 [25] As an example, the kilning temperature has a significative impact on the total phenolic  
117 content (TPC) of the malt with higher values (4 fold) [8] [26] recorded for paler malts with lower  
118 KT. [27] [28] The mashing conditions allow to reduce carbohydrate content from 65 to 49 % by  
119 extracting most of the fermentable sugars leaving cellulose and hemicellulose behind. [15]  
120 However, the remaining composition with high moisture content (75-80 %) is particularly  
121 vulnerable to bacteria, yeast and mould development. [25] LCB compositions such as BSG are  
122 usually determined through fractionation and include: cellulose, hemicellulose, lignin,  
123 protein, lipids and ashes [29], with a C:N ratio of 13.9 for BSG. [30] A meta-analysis of articles  
124 and reviews from the literature was conducted, gathering up to 38 references and the middles  
125 values alongside minimal and maximal percentage values are reported in Table 1 for BSG's  
126 composition (percentage of dry matter). [8] [10] [16] [27] [31] [32] [33] [34] [35] [36] [37] It can  
127 be observed that for each fraction of BSG's lignocellulosic matrix, the percentage can go from  
128 simple to double, which confirms the high variability of its composition. However, it can be  
129 an advantage as the selection of a certain malt type and extraction condition can yield to a  
130 tailored composition richer in one or several fractions of interest, improving the potential  
131 valorisation for a specific fraction.

132 **Table 1** Meta-analysis of mass composition of BSG's dry matter (DM) gathered from up to 38 references.

Fraction	Middle value (%DM)	Number of references	Range (%DM)
Hemicellulose	28.8	24	19.2-40.4
Cellulose	21.3	23	12-26.2
Protein	22.3	38	14.5-24.7
Lignin	15.7	32	4-18.2
Lipids	8.1	18	3.9-13.3
Ash	3.8	34	1.2-4.9

133  
134 Overall, despite the extraction of fermentable sugars during the mashing process, the  
135 main fraction ( $\approx 50\%$ ) of BSG is composed of carbohydrate with hemicellulose and cellulose.  
136 Hemicellulose itself can represent up to 40.4 wt% of the dried biomass and is exclusively

137 composed of **arabinoxylanes (AX)** with a **xylose/arabinose ratio of 7:3, considered as rare**  
138 **sugars**. [10] [27] [34] [38] [39] [40] The third fraction of BSG is proteins (15-25 %DM), [37]  
139 mainly composed of hordein, gluten, globulin and albumin [41], with a composition of amino  
140 acids that greatly varies between pale and dark malt. [42] Extracted proteins from BSG (104.2  
141 mg/g<sub>BSG</sub>) [43] were degraded in enzymatic conditions (*Aspergillus niger*) yielding 17 amino  
142 acids with the most prominent being valine, alanine, phenylalanine, tryptophan and proline.  
143 [44] BSG is also composed of a non-negligible fraction of lignin, followed by a smaller amount  
144 of lipids with a fatty acid profile dominated by linoleic acid (47%) and palmitic acid (32%). [36]  
145 BSG presents a high proportion of TPC (1735 µg/g), vitamins (64 µg/g), and minerals (8588  
146 µg/g) [8], justifying the interest for its use in human and animal feed. However, a strategy that  
147 would allow the complete valorisation of this by-product for higher-value products while  
148 using the intrinsic antioxidant/inflammatory/cancerous properties would be of prime interest.

### 149 **3 Applications**

150 Before focusing on the use of BSG for polymer and composite materials, a quick  
151 overview of the alternative applications will be presented. Thanks to its interesting  
152 composition, rich in protein, minerals, vitamins and TPC, BSG is a by-product of the agri-food  
153 industry that is interesting for human food or animal feed. [45] However, the price of BSG has  
154 to be very low to match standard prices for these applications which can be challenging when  
155 considering drying and transport costs; alternative higher-value valorisation routes would be  
156 preferable. [8]

- 157 • **Animal feed:** Wastes from the agri-food industry only represent 5 % of the animal feed  
158 market but the use of BSG for such an application allow the valorisation of considerable  
159 volumes of this by-product from the brewing industry. Its use (20-30 wt% dry matter) for  
160 cattle has shown significant improvement in milk yield but requires the use of additives to  
161 prevent contamination and improve preservation. [46]
- 162 • **Human food:** Despite the variation of its composition, BSG always contains high amount  
163 of fibres, proteins, minerals, antioxidants, lipids and vitamins useful for human  
164 consumption. [47] BSG can be crushed and mixed by extrusion to prepare flour, [48] for  
165 fibre and protein-enriched pastas [49], added in biscuits, bread, etc. [50] Cookies baking  
166 using fresh BSG is a popular valorisation of this by-product amongst home brewers. [4]

167 Protein hydrolysate have displayed antioxidant and anti-inflammatory activities and could  
168 be used as bioactive edibles. [41]

- 169 • **Heat generation:** The most efficient way to use BSG for combustion application is under  
170 pellet form and could be used directly as fuel for heat production in microbreweries. [51]  
171 Its calorific value equals **9.6-11.3 MJ/kg** [54], similar compared to other bio-fuels for  
172 combustion. [19] However, this requires a costly preliminary drying step and its  
173 combustion liberates particles and toxic gases: NO<sub>x</sub> and SO<sub>x</sub>, 480 and 1000-3000 mg/m<sup>3</sup>  
174 respectively. [19] [39] Recently, a hydrochar from BSG was prepared through microwave-  
175 assisted hydrothermal carbonisation, reported with a high calorific value: 32 MJ/kg [52],  
176 alongside a bio-oil fraction (26 MJ/kg) and a saccharide-rich aqueous fraction. [53]
- 177 • **Other applications:** The valorisation of BSG for the production of biodiesel, biogas,  
178 bioethanol, biohydrogen or biobutanol has recently attracted the interest of the scientific  
179 community. [51] Otherwise, its carbonisation followed by an activation allows the  
180 production of activated charcoal. Other reported usage of BSG mention paper production,  
181 as adsorbent for pollutant and dyes elimination in water, substrate for microorganism and  
182 yeast, fungi growth or as soil fertilisers. [39] [54]

183 Finally, BSG can be chemically valorised into higher-value building blocks to be used as  
184 monomers for polymer synthesis or organic compounds. The focus of this review will be on  
185 the obtention of such building blocks as well as their use in polymer chemistry. Additionally,  
186 BSG can be used as natural filler for composite material applications when mixed with  
187 polymer matrixes.

## 188 **4 Biomass fractionation**

189 Lignocellulosic biomasses (LCB) are appealing raw materials than can yield various  
190 amounts of hemicellulose, cellulose, lignin or protein but their fractionation into compounds  
191 of interest can be challenging, due to the strong entanglement of those fractions. More  
192 specifically, cellulose shows a higher resistance to extraction and degradation (hydrolysis)  
193 treatments due to its crystalline/semi-crystalline nature. Table 1 gathers the compositions of  
194 38 references showing middle values and percentage ranges of BSG composition (dry matter).  
195 [8] Unlike some of the other renewable lignocellulosic materials, the production of BSG is not  
196 in competition with the food sector as it is a waste from the agri-food industry. [55]



197 Furthermore, its **lower matrix density** allows for **more efficient extractions** in **milder**  
198 **conditions**.

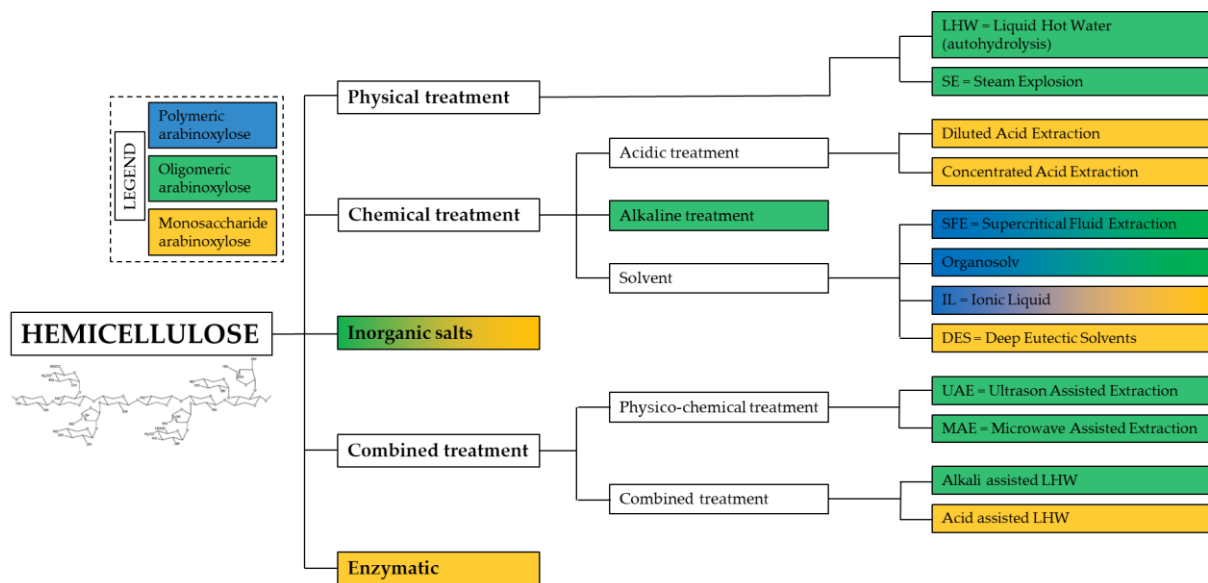
199 LCB fractionation has been widely studied using various strategies depending on the  
200 starting material and targeted fraction but still represents an important challenge for an  
201 efficient valorisation of biomass and the development of biorefineries. After reviewing the  
202 available conditions for the extraction and degradation of each component of the  
203 lignocellulosic matrix, several examples of biomass full fractionation will be presented in  
204 section 4.6, focusing on BSG biomass or similar ones such as wheat straw. A stronger focus  
205 will be placed on the treatment of hemicellulose due to its easier extraction thanks to the easily  
206 extractable and degradable amorphous nature of this polymer, yielding interesting building  
207 blocks. [40]

#### 208 **4.1 Hemicellulose extraction**

209 Hemicellulose extraction has been extensively investigated throughout the fractionation  
210 of various LCB and available conditions for BSG or similar biomasses are summed up within  
211 Figure 2 alongside a brief description of their advantages and disadvantages listed in Table 1.  
212 These processes include liquid hot water (LHW) also called autohydrolysis, steam explosion  
213 (SE), alkaline treatment, organosolv, ionic liquids (IL), deep eutectic solvents (DES),  
214 supercritical fluids (SFE), enzymatic extraction, ultrasonic- and microwave- assisted extraction  
215 (UAE and MAE) and finally diluted and concentrated acidic treatment (DAE and CAE  
216 respectively). The mechanisms of hemicellulose breakdown have been investigated by Lu et  
217 al. [56] but most of the conditions only extract hemicellulose under polymeric form or slightly  
218 degraded to oligomers or suffer from toxicity and yields limitations for example. The last two  
219 treatments presented (acidic conditions) are known to be most efficient for the complete  
220 breakdown of the hemicellulose to the monosaccharides units which is more interesting to  
221 obtain building blocks for polymer synthesis purposes and will thus be studied in more detail  
222 below.

223 Even though monomeric saccharides are more promising for polymer application, it was  
224 shown that oligomers of xylose also exhibited high potential. Mensah et al. recently reviewed  
225 the potential of xylo-oligosaccharides (XOS), ideally recovered after LHM pre-treatment of  
226 LCB (sugarcane in their case) showing a higher resistance compared to other reported  
227 oligosaccharides. Thanks to its good anti-microbial/infection/inflammatory/cancerous and

228 prebiotic properties, XOS are promising for applications in pharmaceutical, food and cosmetic  
 229 sectors. [57]  
 230



231  
 232 **Figure 2** Different hemicellulose extraction processes with the form of the final product (polymeric,  
 233 oligomeric or monosaccharide).

234 **Table 1** Summary of available hemicellulose extraction processes alongside their advantages and  
 235 disadvantages.

Treatment	References	Arabinoxylose form	Selectivity and efficacy
LHW	[56] [58] [74]	Oligomeric	High yield and selectivity: low amount of glucose. Autohydrolysis at pH=4-7 when acetic acid is liberated (160-240°C). No corrosion problem but post-treatment required to obtain monosaccharides.
SE	[58] [59]	Oligomeric	Similar to LHW (200-240 °C and high pressure) with higher efficacy but lower selectivity (lignin dissolution) and requires acidification of the matrix.
DAE	[60] [56] [58] [59] [40] [61] [73] [62] [63] [64]	Monosaccharide	Most efficient conditions to obtain monosaccharides from hemicellulose. Up to 96 % of AX recovered and most of the proteins (up to 90%, easily precipitated). Part of the carbohydrates can be degraded into furanic moieties or humines.
CAE	[60] [56] [58] [59] [40] [61] [73] [62] [63] [64]	Monosaccharide	Similar to DAE but suffers from stronger degradation of carbohydrates and corrosion problems due to highly acidic conditions. More useful for cellulose breakdown as it is tougher to disassemble than hemicellulose.

<b>Alkaline treatment</b>	[56] [65]	Oligomeric: 49200-64300 g/mol	Saponification at 80-150 °C between ferulic acid from lignin and AX, liberating hemicellulose in high yields.
<b>SFE</b>	[4] [56] [66]	Polymeric/ oligomeric	70-80% Yield but with high amount of degraded products (like humines) using supercritical CO <sub>2</sub> (40°C, 175 bar) or subcritical water (200-260°C). Possible to obtain aromatic moieties through hydrothermal carbonisation.
<b>Organosolv</b>	[56]	Polymeric/ oligomeric	Use of DMSO or dioxane. Poor selectivity and suffers from toxicity, flammability and ecotoxicity issues. Ethanol organosolv treatments seem more efficient for lignin or cellulose extraction.
<b>IL</b>	[67] [58]	Polymeric/ monosaccharide	[Amin]Cl used to break H-bonding and liberate AX (75 % yield) under polymeric form except for [C <sub>2</sub> mim][OAc] liberating monosaccharides. Difficult to separate products and IL to regenerate them.
<b>DES</b>	[23] [56]	Monosaccharide	ChCl/Glycerol DES exhibit low selectivity: degradation of cellulose. Replacing glycerol by lactic acid or urea allows to separate the extracted cellulose.
<b>UAE</b>	[56] [68] [69] [70]	Polymeric/ oligomeric	Combination with alkaline conditions to obtain oligomers, polymers or fermentable sugars for bioethanol production (75 % AX yield on oat).
<b>MAE</b>	[56] [71]	Oligomeric	More efficient extraction than UAE: 1-5 min vs 10-30 min for UAE (77 % yield).
<b>Inorganic salts</b>	[58]	Oligomeric	Alternatives to acidic hydrolysis with less corrosion and recyclability issues using NaCl, KCl, CaCl <sub>2</sub> , MgCl <sub>2</sub> , FeCl <sub>2</sub> , ZnCl <sub>2</sub> , FeSO <sub>4</sub> , FeCl <sub>3</sub> (89 % yield).
<b>Enzymatic</b>	[72] [73]	Monosaccharide	Preferably used for cellulose degradation as simpler methods are known for hydrolysis of hemicellulose. Still investigated to eliminate AX before alkaline extraction of proteins in BSG, or for prebiotic application. Also, the presence of enzymatic inhibitors within the lignin fraction is an impediment on hemicellulose degradation using enzymes. [40]

236

## 237 4.2 Saccharification of BSG (hemicellulose acidic treatment)

238 **Diluted and concentrated acidic extraction (DAE and CAE respectively)** allow the  
239 breakdown of hemicellulose into monosaccharide. Even though **stronger acidic conditions**  
240 improve the homogeneity of the reaction and allow the use of lower temperature and pressure,  
241 [40] it faces corrosion, acidic waste management and stronger degradation issues converting  
242 sugars into furanic moieties or humines. [61] Even though this decomposition can be slowed  
243 by adding protectors such as ethyl-ethyl ketone [40], these conditions are typically used for  
244 the more robust crystalline carbohydrate polymer, cellulose, to produce glucose using 10-30  
245 % H<sub>2</sub>SO<sub>4</sub> for example. These conditions can even be used to directly produce furanic derivatives  
246 and optimised using MAE or UAE. [40]

247 A wide range of acids have been investigated to hydrolyse hemicellulose and are listed  
 248 in Table 2 alongside their specificities and advantages. [40] [56] [58] [74] [75] Overall, sulfuric  
 249 acid is found to be the most efficient and selective catalyst for acidic hydrolysis with the  
 250 highest monomeric xylose and arabinose yields while leaving the cellulose in the solid fraction.  
 251 [58] The **combined severity (CS)** evaluates the severity of a treatment using time, pH and  
 252 temperature. Highest xylose yields are obtained for low severity (CS<2-3) while higher values  
 253 increase saccharides degradation into furanic compounds (furfural for pentose and 5-HMF for  
 254 hexose), confirming the use of DAE for optimal saccharification. Even higher CS will  
 255 dehydrate carbohydrates further to form pseudo-lignin increasing the amount of Klason's  
 256 Lignin. [61]

257 **Table 2** List and advantages of acids used for the extraction and saccharification of BSG's hemicellulose.

Acid	Specificity and advantages
H <sub>2</sub> SO <sub>4</sub>	Best reactivity and selectivity
HCl	Reactivity similar to sulfuric acid but lower selectivity (glucan dissolution): preferred for cellulose degradation
HNO <sub>3</sub>	Increased degradation into furan derivatives
Trifluoroacetic	Increased degradation into furan derivatives
Oxalic	Selective hydrolysis of arabinose from the xylose backbone at low concentration (0.5-2 wt%)
Maleic	High yield (95.5 %)
<i>p</i> -Toluene sulfonic	Increased solubility
Super acids	C-SO <sub>3</sub> OH (carbon-based solid acid): allows the use of reduced temperature, water usage and corrosion issues
Phosphoric	-
Formic	-

258 To better understand hydrolysis of polysaccharides into monosaccharides, Maki-Arvela  
 259 et al. [40] have studied the kinetics and mechanisms to optimise reaction conditions for  
 260 improved yields and reduced amounts of degradation products (furans and humines). The  
 261 mechanism is either based on the protonation of glycolic bond or the pyranic oxygen and the  
 262 kinetics are dictated by their structures with  $\beta$ -anomers showing weaker tension, such as  
 263 arabinose. **Reactivity** can thus be ordered increasingly as such: **glucoside < mannoside <**  
 264 **galactoside < xyloside < arabinoside**, in accordance with the selectivity observed with diluted  
 265 oxalic acid hydrolysis. However, higher reactivity also implies higher risk of degradation

266 chain: xylan → xylose (oligomeric) → xylose (monomeric) → furfural → humines, [60] as well  
267 as the formation of side products such as levulinic and formic acids justifying the use of low  
268 amount of acidic catalyst. [40]

269 One **advantage of BSG** compared to other LCB, apart from its high availability and low  
270 price, is the composition of its hemicellulose exclusively made of **rare sugars**: [40] **xylose and**  
271 **arabinose with a 7:3 ratio**, similar to wheat straw but very different from hard and soft wood  
272 that are mainly composed of glucuronoxyllane and galactomannane. Furthermore, its **main**  
273 **advantage is the lower density of its matrix**, making its hemicellulose extraction easier and  
274 more efficient: 37 minutes for BSG against 12 hours for hard wood in similar conditions. This  
275 increased reactivity is due to the lower apparent activation energy of agri-food wastes  
276 estimated at **50 kJ/mol** (wheat straw) against 100-200 kJ/mol for wood derivatives, resulting in  
277 lower operating temperatures: **100-200°C** against 150-250°C. However, stronger degradation  
278 into furan derivatives can be observed when comparing corn and pine biomass for example  
279 which require the need of milder reaction conditions. [40] It is noteworthy to mention that the  
280 use of continuous flow saccharification developed by Harris et al. allows to avoid the  
281 degradation of the monomeric sugars. [76] In the end, BSG was found to be the **most**  
282 **interesting raw material for lignocellulosic fractionation** and hemicellulose hydrolysis when  
283 comparing various biomasses (hard wood, soft wood and several agricultural wastes), with a  
284 xylose yield around 95 % (similar to wheat straw) and requiring the **lowest temperature and**  
285 **reaction time**. [40] Finally, the extracted sugars can be separated, after filtration of the salts  
286 from the acid catalyst, using ionic exchanger resins for example, [40] but it is best to use the  
287 mixture of sugars if possible to reduce the number of steps and environmental impact of  
288 purification and separation procedures. The use of **BSG as bioresource** for the obtention of  
289 hemicellulose or monosaccharides is thus competitive compared to other biomasses, allowing  
290 higher yields and the use of milder reaction conditions and shorter reaction time, leading to  
291 **greener processes**.

### 292 **4.3 Protein extraction**

293 The protein fraction in LCB is usually easy to extract, especially for BSG that has a softer  
294 matrix. An example of mild conditions is described by Connolly et al. where BSG was put in  
295 the presence of water at 60°C for 18 hours before centrifugation and precipitation at -20°C. [42]

296 One of the interesting findings is the nature of the proteins with larger profile for pale BSG (59  
297 % > 10 kDa) compared to black BSG (6 % > 10 kDa) and a high antioxidant profile thanks to a  
298 high TPC. Vieira et al. used a more sequential approach for protein and arabinoxylan  
299 extraction under basic conditions. Each hemicellulose extract was then acidified using citric  
300 acid (pH = 3) precipitating the proteins, recovered by filtration. The acid was then recovered  
301 by precipitation in ethanol to yield oligomeric arabinoxylose. [77] Optimised extraction  
302 conditions were investigated using UAE yielding high amount of proteins from BSG (104.2  
303 mg/g<sub>BSG</sub>) [43] and subsequently 17 amino acids after enzymatic lyse. [44] Du et al. reviewed  
304 protein extraction conditions on different biomasses including BSG and cyanobacteria  
305 (*Arthrospira platensis*, AP). [78] Three conditions were investigated with the LHW as standard,  
306 alkaline treatment as milder conditions (40°C) and subcritical method (200°C, 40 bar) as  
307 greener method with an extraction time of 20 minutes but at an increased cost. The highest  
308 protein extraction yield was obtained with alkaline treatment: 21.4 wt% for BSG and 55.5 wt%  
309 for AP with purities of 60.2 and 68.8 wt% respectively with the rest of the extract being mainly  
310 composed of oligomeric hemicellulose or traces of cellulose. Proteins can also be extracted with  
311 similar efficiency in acidic conditions as described by Babu et al. [79] Another approach by  
312 Sajib et al. or Niemi et al. is to remove the hemicellulose fraction enzymatically in order to  
313 extract proteins from BSG without saccharides in alkaline conditions. [34] [72] The  
314 simultaneous recovery of proteins and carbohydrates is also possible by using a mixture of  
315 carbohydrase and peptidase yielding hydrolysates to be used as prebiotic food supplement  
316 for example. [80]

317 As explained previously, the reported use of BSG is systematically performed on dry  
318 BSG for transportation and preservation purposes mainly, but this drying step comes with a  
319 non-negligible environmental cost. [18] Tackling this issue, Connolly et al. proposed a more  
320 sustainable valorisation using wet BSG yielding protein-rich hydrolysate (< 5 kDa), with a  
321 different amino acid composition reported between pale and dark malt. To overcome the non-  
322 grinded nature of wet BSG, compared to the dry one that is easily shredded, the agitation was  
323 performed by an Ultra Turrax, to reduce particles size while keeping a good homogeneity. [42]

324 To summarise, protein extraction can be achieved easily using several methods.  
325 However, if the high amount of protein is the fraction of interest for food application, the other  
326 fractions (fibres, vitamin, minerals) comprised in BSG could be of interest, [41] [46] [47]

327 rendering the extraction potentially obsolete. Other possible applications for this protein  
328 fraction or hydrolysate lies in the cosmetic sector where such compounds from wheat and oat  
329 are already used for their moisturizing and nutritive properties. [81] Protein extract could also  
330 be used for edible film production out of prolamin, or for composite materials using BSG's  
331 hordein. [22]

#### 332 **4.4 Lignin extraction**

333 The high content in phenolic compounds could be interesting for the design of active  
334 packaging through intrinsic antioxidant properties or to mitigate the effect of oxidative stress  
335 in nutraceuticals, cosmetic or medical application (anti-inflammatory, anti-atherogenic, anti-  
336 cancerous). [82] Standard measurement of TPC (Folin-Ciocalteu reagent) gives TPC values of  
337 3-4.7mg<sub>gal</sub>/g<sub>BSG</sub> (gallic acid equivalent) [26] [83] and phenolic compounds (hydroxycinnamic  
338 acids), corresponding to 1-2 wt% of BSG, are mainly represented by ferulic acid. [35] These  
339 hydroxycinnamic acids are usually extracted through hydrolysis in basic conditions, [84]  
340 whereas the best results were reported using enzymatic lyse yielding 4.61 mg/g<sub>BSG</sub>. [72] [85]  
341 Even though UAE extraction does not improve extraction yields, [26] an increase in  
342 temperature (>160 °C) yields higher extraction efficacy which increases the antioxidant  
343 activity. [86]

344 As lignin is a tough fraction of the LCB, often intertwined with the cellulose fraction, it  
345 is often extracted in the later stages of the fractionation process. A standard way to recover  
346 lignin is its extraction in basic conditions followed by a reacidification to force its precipitation.  
347 This method is used by Mussatto et al. with a soda pulping process on BSG followed by the  
348 addition of sulfuric acid in the black liquor. Different pH conditions were experimented with  
349 the best conditions yielding 81 % of the solubilised lignin. [87] Using a different strategy,  
350 Niemi et al. described an optimised protocol in 3 steps with first, the enzymatic degradation  
351 of carbohydrates, then the enzymatic lyse of proteins, followed by their precipitation in HCl,  
352 yielding a solution rich in lipids and lignin under the degraded form of lignan. [34] Cassoni et  
353 al. investigated the use of DES for lignin extraction from BSG and olive tree pruning (OTP),  
354 with a higher antioxidant power reported for the latter. Good lignin yields (54.5 % for BSG and  
355 37.8 % for OTP) were obtained with purities over 75 % and similar M<sub>w</sub> using a lactic acid (LA)  
356 and choline chloride (CC) (5:1) mixture as DES for the delignification process. [88] Gbenebor  
357 et al. used diethyl ether to remove extractable, before degrading carbohydrates (cellulose and

358 hemicellulose) in strong acidic conditions (10 M of H<sub>2</sub>SO<sub>4</sub>, HCl or acetic acid) and 5M NaOH  
359 and filtration, with the highest purity (98 % purity) and yields (82.9 % of the lignin contained  
360 in BSG, representing 5.6 wt% of the original composition) obtained when using H<sub>2</sub>SO<sub>4</sub>. [89]  
361 Characterisation of the extracted lignin showed good thermal stability with a T<sub>g</sub> of 107 °C  
362 (H<sub>2</sub>SO<sub>4</sub>). Finally, organosolv treatment is a possible procedure to recover the degraded lignin  
363 within a black liquor. This was described by Parchami et al. after an acidic pre-treatment to  
364 eliminate the glucan-rich fraction. [90] The organosolv process conditions were optimised  
365 using 50 % v/v ethanol to obtain precipitated lignin with a 58 % yield and a 95 % purity.

366 Thus, lignin is a fraction more difficult to extract with multiple steps necessary. In  
367 addition to its difficult extraction or dissolution, the presence of its aromatic components  
368 showed microbial inhibition for the transformation of xylose to xylitol. [40] Furthermore, BSG  
369 is not the optimal biomass to be selected if the fraction of interest is lignin, as barley shows a  
370 significantly lower lignan content compared to other cereals such as rye or wheat. [91] Finally,  
371 the use of lignin or building blocks from lignin for polymer synthesis usually yield higher  
372 resistance materials thanks to its aromatic backbone but these materials show lower  
373 biodegradability profile compared to other biopolymers from carbohydrates for example. [22]

#### 374 **4.5 Cellulose extraction**

375 Few examples of cellulose extraction and valorisation from BSG are found in the  
376 literature due the more complex accessibility, especially opposed to BSG's hemicellulose,  
377 being the most easily extractable compared to other biomasses, and simple to convert to  
378 monomers of rare sugars. Matebie et al. used a conventional approach for the obtention of  
379 cellulose with 3 pre-treatments to remove hemicellulose and lignin: diluted acid hydrolysis,  
380 alkaline treatment, and bleaching. [92] The obtained cellulose was then converted into CNC  
381 (Cellulose NanoCrystals) using concentrated acid hydrolysis (51 wt% H<sub>2</sub>SO<sub>4</sub>). The synthesis  
382 parameters were optimised to yield cellulose with 43.24 % and a high crystallinity.

383 Marki-Arvela et al. reviewed the conditions reported for the extraction and hydrolysis  
384 of cellulose. Due to its resilience, most available methods suffer from drawbacks such as  
385 corrosion and waste management issues for strong acids or the need of high temperatures for  
386 mild acids, both leading to significant dehydration of sugars, whereas the use of mineral acids  
387 generates large amounts of salts after the neutralisation steps. Physical (ball milling, grinding,



388 steaming) or chemical treatments (SFE) can be applied to soften the crystalline structure (rated  
389 as CrI for Crystallinity Index) to amorphous cellulose, showing how resilient this fraction is,  
390 compared with hemicellulose. An alternative method to produce glucose from cellulose are  
391 the vapours of HCl at 0°C. [40] One of the most efficient way to valorise cellulose is through  
392 enzymatic hydrolysis, in comparison with hemicellulose that can be more easily degraded  
393 with simpler conditions and where a microorganisms inhibitors are still present which lowers  
394 the efficiency of such enzymes. [40] With a similar approach than Lynch et al. [73] with the  
395 saccharification of the carbohydrate fractions from BSG using a cocktail of enzymes, Maache-  
396 Rezzoug et al. focused more on the degradation of cellulose into glucose (48 g/100 g<sub>BSG</sub>)  
397 alongside arabinose and xylose production (5 and 9 g/100 g<sub>BSG</sub> respectively). They used  
398 Cellulast, a mixture of 4 types of enzymes to saccharify cellulose, after an instantaneous  
399 controlled pressure drop process (DIC, an optimised SE) pre-treatment. [93] Similarly, Mishra  
400 et al. pre-treated BSG in alkaline conditions before bleaching to produce cellulose nanofibrils  
401 (CNF), showing lower crystallinity than the CNC described above. [94]

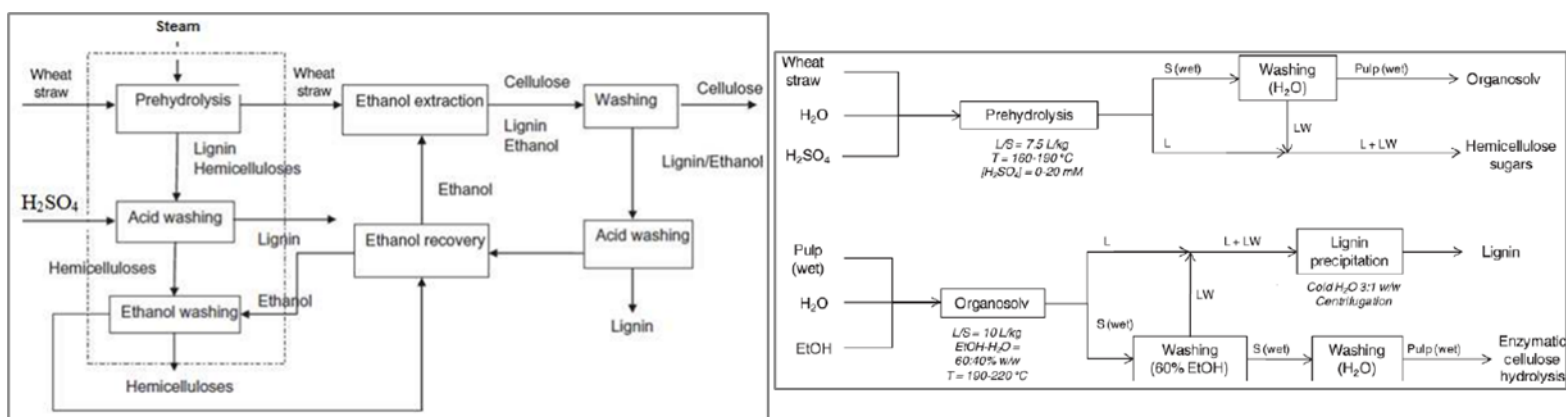
402 The main applications reported in the literature for BSG's cellulose are its use for ethanol  
403 production or as substrate for enzymes, yeast or fungi growth. However, higher value  
404 applications, such as CNC are preferred for cellulose and most of the time for these  
405 applications, only the cellulose containing fraction is utilised, whereas a complete use of the  
406 fully fractionated LCB would be preferred, economically and environmentally.

#### 407 **4.6 Biomass full fractionation**

408 LCB fractionation has been widely studied using several strategies depending on the  
409 type of biomass used and the fraction of interest, but for optimal comparability, only BSG or  
410 similar biomass (wheat straw or corn stalk) will be reviewed. As detailed previously (4.1),  
411 hemicellulose is easily separated by mild pre-treatments thanks to its amorphous nature which  
412 liberates and exposes lignin and cellulose that require stronger conditions to be separated  
413 and/or degraded. Like for BSG's dewatering, the use of mechanical treatment is preferred to  
414 soften the matrix, reducing the environmental impact of such fractionation. [99]

415 Two examples of full fractionation of wheat straw biomass were described by Ortega et  
416 al. [67] et Liu et al. [95] and are shown below (Figure 3). In both cases, a pre-hydrolysis was  
417 performed to isolate hemicellulose. For Liu et al., a DAE allowed to obtain it selectively while

418 Ortega et al. recovered a part of the lignin fraction that had to be separated from the oligomeric  
 419 hemicellulose by the less selective steam extraction. Nevertheless, a simple acid washing  
 420 results in the precipitation of lignin to recover hemicellulose. After its removal, the rest of the  
 421 matrix was subject to organosolv procedure to separate lignin and recover cellulose. For the  
 422 latter, it was hydrolysed using enzymes by Liu et al. to break it down to saccharides. [95] The  
 423 economic feasibility of such a biorefinery has been studied and would yield hemicellulose with  
 424 an estimated price of 0.05 €/kg.



426 **Figure 3** Lignocellulosic biomass fractionation flow chart (wheat straw) described by Ortega et al. (left)  
 427 [67] et Liu et al. (right) [95] to separate hemicellulose, lignin and cellulose.

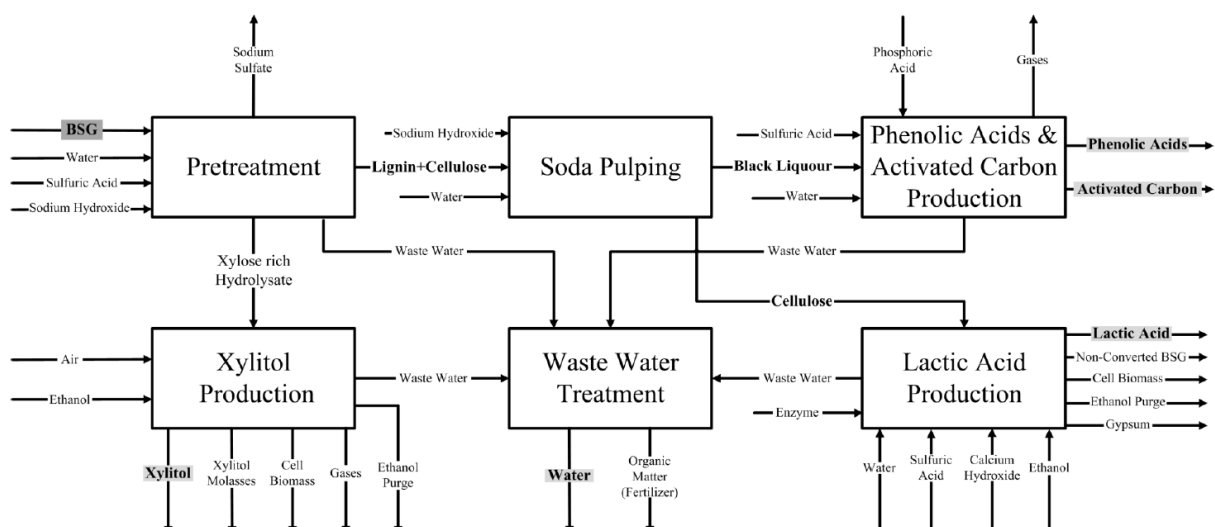
428 When studying the fractionation of corn stalk biomass, Zhang et al. have shown that the  
 429 separation of lignin and cellulose (UAE in ethanol in their case) was strongly impacted by the  
 430 pretreatment method used for hemicellulose extraction. [96] Indeed, after the LHW  
 431 pretreatment, an alteration of the lignin matrix resulted in its repolymerisation during the  
 432 cooling step, forming films around the cellulose fibers rendering their separation more  
 433 difficult. The shift to a DAE or organosolv pretreatment to recover hemicellulose solved this  
 434 issue. [96] To ease this tedious separation between lignin and cellulose, HIUS (high intensity  
 435 sonication) softened the matrix for a more efficient liberation of cellulose. [97] A larger-scale  
 436 (1 ton) fractionation of BSG was reported by de Crane d'Heyselaer et al. [98] to produce  
 437 cellulose and lignin biopolymers in a 3-step process with respective yields of 50.1 and 41.8 %.  
 438 These polymers could in turn be further degraded into building blocks of interest for  
 439 packaging application through film forming for example.

440 From all the condition reviewed for each fraction and examples of full fractionations of  
 441 LCB described, it can be concluded that various approaches are available depending on the

442 biomass used (milder conditions required for BSG for example) and the targeted form of the  
 443 fraction (polymeric, oligomeric, monomeric). Furthermore, the conditions used for each step  
 444 might significantly influence the following extraction conditions efficiency. When selecting the  
 445 process conditions for each step of the fractionation, it is important to keep in sight the form  
 446 of the fraction that is desired as well as the potential degradation of each component, especially  
 447 for carbohydrates that can be converted into furanic derivates or humines.

## 448 5 Building blocks from BSG

449 Few examples of chemical valorisation of BSG are reported in the literature with a full  
 450 fractionation of BSG to obtain various building blocks of interest, as developed by Mussatto et  
 451 al. and described below. [16] [99] As displayed in Figure 4, a DAE was used as an efficient  
 452 mild pre-treatment using citric acid to extract 91.8 % of hemicellulose under monosaccharide  
 453 form, yielding a xylose-rich hydrolysate. This fraction was in turn converted to xylitol with a  
 454 97.8 % yield, while the rest of the LCB was treated in alkaline solution for delignification,  
 455 yielding phenolic acids and activated carbon after phosphoric acid activation and  
 456 carbonisation. [16] The cellulose-containing solid fraction was fermented using *Lactobacillus*  
 457 *delbrueckii* to transform 99 wt% of the glucose into lactic acid (LA) after adjusting the pH for  
 458 optimal yield. [99] The economic feasibility of this strategy was validated by the biorefinery  
 459 modelisation giving an economical margin of 62.25 % with a PEI (Potential Environmental  
 460 Impact) of the process of 0.012 PEI/kg and a carbon footprint of 0.96 kg CO<sub>2</sub>-e/kg of BSG. [16]  
 461 This shows the potential of BSG as LCB to be chemically valorised, especially for polymer  
 462 chemistry where these building blocks could be of high interest.



463

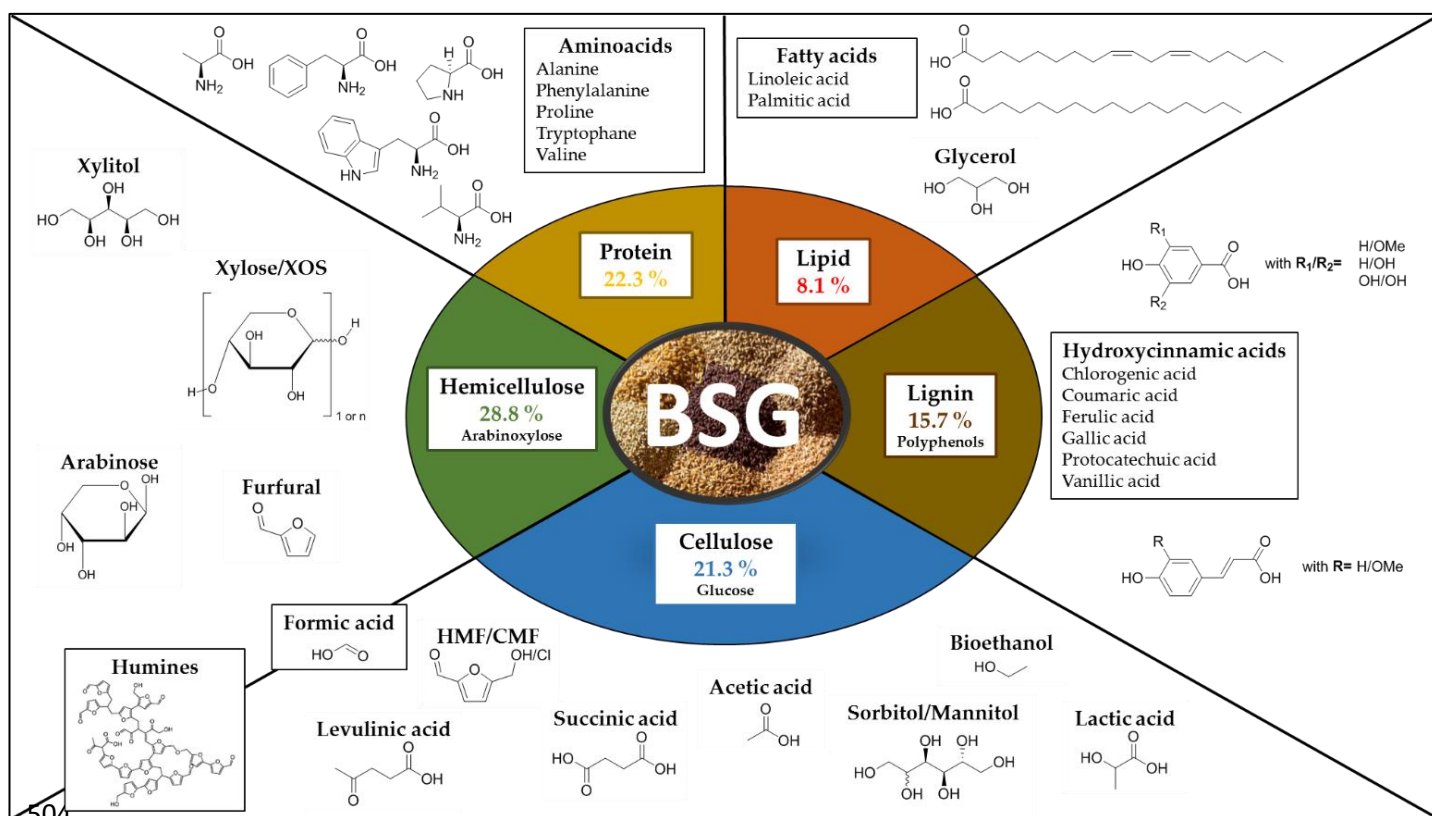
464 **Figure 4** Full fractionation flowchart of BSG yielding various building blocks proposed by Mussatto et  
465 al. [16]

466 The extraction and degradation of hemicellulose offers the possibility to obtain various  
467 compounds of interest. Swart [93] described an optimised pretreatment between the LHW and  
468 SE, namely hydrothermal treatment (HTT), allowing the use of lower operating temperature  
469 and dilution to obtain either xylose oligosaccharides (XOS) with a yield of 76.4 % or xylose  
470 from BSG's hemicellulose. [100] Xylose could in turn be transformed into xylitol through  
471 catalytic hydrogenation or microbial conversion, to be used for anti-inflammatory, anticaries  
472 or sweetening applications. Otherwise, xylose can directly be degraded into furfural and  
473 ultimately into formic acid. [40]

474 The cellulose fraction can be degraded through glucose into a myriad of molecules such  
475 as sorbitol and mannitol, obtained by heterogeneous catalysis with Ni or Ru [40] or through  
476 hydrogenation of cellulose. These could be used as sweetener, for vitamin C synthesis, or  
477 converted to isosorbide, sorbitan, glycols, glycerol, lactic acid or sorbose. [40] Alternatively,  
478 the glucose obtained from cellulose could be converted into HMF or CMF and then into formic  
479 and levulinic acid. [40] Another reported obtention of building blocks from BSG's cellulose  
480 was given by Akermann et al. with an optimised fermentation using *Cellulomonas uda* to  
481 produce a mixture of succinate, lactate and formate in small quantities (< 5 g/L) alongside  
482 larger quantities of ethanol and acetate (> 25 g/L) with a global liquid product yield of 0.41  
483  $g_{\text{prod}}/g_{\text{BSG}}$ . The ethanol to acetate ratio could be increased significantly by adapting the pH. [101]

484 The overview of all building blocks obtainable from BSG's lignocellulosic biomass (LCB)  
485 according to the literature so far are displayed in Figure 5. The other minor fractions could  
486 lead to phenolic acids from lignin, hydroxycinnamic acids more specifically, fatty acids and  
487 glycerol from the lipid fraction and various amino acids from the protein fraction. A few  
488 techno-economic analyses have assessed the feasibility for several building blocks (xylitol,  
489 protein, lactic acid) or biopolymers productions showing the competitiveness of BSG's  
490 valorisation thanks to the low price of the biomass and softness of its matrix, allowing simpler  
491 fractionation procedures and functionalisation. [16] [22] [102] Some of the building blocks  
492 described here can be viewed as **platform molecules**, allowing the obtention of a wide range  
493 of components. More specifically, furan derivatives obtained from the hemicellulose and

494 cellulose fractions are known to be promising platform molecules thanks to their well-  
 495 documented and efficient production from carbohydrate and versatility of compounds  
 496 obtainable through simple chemical transformations. Compounds of interest obtained from  
 497 furfural and hydroxymethyl furfural (HMF) are furan-2,5-dicarboxylic acid (FDCA), diformyl  
 498 furan (DFF), 5,5'-oxy-bis(methylene)-bis-2-furfural (OBMF) [103], 2,5-  
 499 bis(hydroxymethyl)furan (BHMF) to name but the most prominent ones, as well as various  
 500 linear diacids, diols and amine derivatives. [104] [105] These molecules are of high interest for  
 501 solvent, fuel, [104] drug synthesis, surfactant synthesis [106] applications as well as monomers  
 502 for polymer synthesis, [107] [108] with FDCA being one of the 12 most promising building  
 503 blocks for green chemistry.



505 **Figure 5** Overview of available building blocks obtainable from the BSG's LCB (percentage of each  
 506 fraction given as mean values: Table 1).

507 Promising examples of BSG biomass fractionation have been described, showing the  
 508 potential of such an application for high valorisation strategies. However, challenges are still  
 509 to be overcome for an optimal valorisation such as efficient scale-up and biorefinery designing,  
 510 to assess the feasibility of complete valorisation of this bioresource, its economic viability and  
 511 environmental impact. Ideally, these chemical routes would use the wet biomass to limit this

512 specific impact. These challenges will have to be addressed in the future to improve the use of  
513 BSG and should be compared to other similar biomasses using comprehensive tools such as  
514 LCA (life cycle analysis).

## 515 **6 Polymers and composite materials from BSG**

516 The synthesis of polymers can be an efficient way to valorise large quantities of BSG or  
517 any biomass waste or by-product when it can be converted into interesting building blocks  
518 such as monomers or oligomers. In turn, such polymeric materials could be produced in vast  
519 amounts, increasing the use of renewable resources and potentially reducing low-value  
520 valorisation applications or landfill of BSG. However, the improvement of the impact of such  
521 valorisation strategies should, if possible, be assessed thoroughly with appropriate tools such  
522 as LCA. [8] At the core of the design of these valorisation strategies should be included as  
523 much parameters as possible for optimal reduction of the environmental footprint: impact of  
524 drying, transportation, volume availability, synthetic pathway in accordance with green  
525 chemistry principles, life of the object, potential recycle, end-of-life treatment, to name but a  
526 few. The use of LCB residue as solid filler for composite material production is another way  
527 to valorise biomass for material production with potentially a lower environmental impact  
528 than polymer production. Indeed, less transformation (extraction, purification,  
529 polymerisation) should be required compared to the synthesis of polymers from BSG-derived  
530 monomers. However, the percentage of fillers that can be incorporated might be limited, as  
531 the materials could suffer from property losses, higher water intake, strong colouration, etc.

### 532 **6.1 Polymers**

533 As hemicellulose is the easiest fraction to recover from the BSG matrix, its use as starting  
534 material for polymer synthesis is an appealing strategy. However, polymeric or oligomeric  
535 hemicellulose exhibit weak properties requiring plasticisation, blending with another material  
536 or chemical modification. [56] One example was proposed by Farhat et al. with an extraction  
537 of polymeric hemicellulose under alkaline conditions, followed by its crosslinking in presence  
538 of zirconium to obtain hydro-resistant gels. [65] Similarly, Lu et al. described the  
539 functionalisation of polymeric hemicellulose through etherification, esterification or  
540 branching using acrylamides (graft copolymerisation). A strategy was presented to improve  
541 hydrophobicity of such polymers by crosslinking hemicellulose using polyacids such as citric,

542 oxalic, maleic or succinic acids. [56] Moreirinha et al. used two fractions of the LCB through  
543 arabinoxylan suspensions from BSG, mixed with NFC (Nano-Fibrillated Cellulose), yielding  
544 films with antioxidant, antibacterial and antifungal properties. [109] Similarly, a combination  
545 of cellulose and polymeric AXs (ArabinoXylans) from BSG can also be used for food packaging  
546 production with good mechanical and thermal stability. [22]

547 Qazanfarzadeh et al. recently reviewed the fractionation of BSG's matrix comparing  
548 various biorefinery strategies with the use of each fraction for films and coatings applications  
549 in the food packaging sector, showing the potential of this promising renewable resource. [22]  
550 The mixture of lignin, hemicellulose and cellulose proved to be difficult to use as such for film  
551 forming application, requiring separation, ideally with high purity to improve the properties  
552 of the respective biopolymers. Thanks to its high intrinsic mechanical and water-resistant  
553 properties, cellulose can be used by itself for film and coating applications or mixed with other  
554 compounds like naringin to improve UV-blocking and barrier properties for example. [110]  
555 Using the cellulosic fraction after its isolation in alkaline conditions followed by bleaching,  
556 Martins dos Santos et al. reported its conversion in a microwave reactor to the functionalised  
557 polymer CMC (Carboxy Methyl Cellulose). [111] The optimised synthesis of the polymer  
558 offered a greener pathway compared to the industrial method with a broad spectrum of  
559 applications for CMC: paper, textile, pharmaceutical, paint and food sector.

560 Apart from carbohydrate fractions of BSG, Lee et al. used proteins from BSG (3 %)  
561 alongside chitosan (2 %), mixed with glycerol to form films with antioxidant and antimicrobial  
562 properties. [112] As reported above (4.3), the protein fraction can also be used for film-forming  
563 applications under their polymeric form, showing promising mechanical and antioxidant  
564 properties when formulated with PEG. [22]

## 565 **6.2 Composite materials**

566 According to the literature, BSG can be used as a replacement of other biomasses such  
567 as sawdust or wood particles for already know composite materials. Several studies have been  
568 reported with BSG introduced as filler for construction materials, such as bricks (3.5-15 wt%  
569 of BSG), [39] or for the production of particle board with unaltered properties if the amount of  
570 BSG is kept below 10 wt%. [113] It was also used as a sawdust replacement for isocyanate  
571 composite materials but resulted in a performance decline with properties being halved due  
572 to BSG's presence. [114] Polyurethane and polyisocyanate foams have also been mixed with

573 16.7 wt% BSG for applications in thermal insulation but the authors focused more on the  
574 polymer matrix properties rather than the impact of the filler. [115]

575 Ferreira et al. designed composite materials from BSG and potato starch by hot pressing  
576 to produce inexpensive natural composite materials, to be compared with EPS (extended  
577 polystyrene). Several BSG percentage were investigated yielding materials with higher  
578 flexural strength and rigidity than the standard EPS. However, it was shown that these  
579 materials were prone to water uptake, drastically reducing their performances. The addition  
580 of a crosslinker, chitosan or glyoxal, or the coating of the produced trays with beeswax were  
581 proposed as innovative strategies and successfully reduced water absorption and avoided the  
582 drop in performances previously observed. [116] Similarly, Hejna et al. developed BSG/Mater-  
583 Bi polymer composites (biopolymers from starch and protein), to improve the resistance of  
584 thermoplastic starch. Even when strengthening the composites by chemical treatment with  
585 diisocyanates, the composites revealed to be very sensitive to water, with weak mechanical  
586 properties and thermal stability despite an improved biodegradability profile. [117] [118]  
587 BSG's fibres (1-5 wt%) were also introduced in starch film by Castanho et al. to improve tensile  
588 strength and thermal stability. [119]

589 BSG can also be used as filler for composite materials using more traditional plastics.  
590 Revert et al. prepared composite materials by extrusion of a PP matrix containing 10-40 wt%  
591 of BSG. The introduction of BSG required a lower operating temperature to avoid combustion  
592 risk, as the degradation observed with TGA was found between 250-350°C. The obtained  
593 material showed lower mechanical resistance compared to neat PP but a higher thermal  
594 stability. Even though water absorption is a common issue when using lignocellulosic fillers  
595 such as BSG, its introduction in the PP matrix revealed only a low absorption (< 6 %). [120]  
596 Further examples can be found with new composite materials being developed by industry,  
597 such as the biodegradable composite materials proposed by Waste Me Up (France) with a PLA  
598 matrix containing 5-30 wt% BSG. However, these materials exhibit a low thermal resistance  
599 with a temperature of use below 50°C. [121] Additionally, BSG can be used in combination  
600 with other fillers for hybrid filler composite materials. This strategy was used by Formela et  
601 al. and Zelder et al. to develop materials using a mix of BSG and GTR (Ground Tire Rubber)  
602 to replace natural rubber or to be introduced in a polyurethane matrix. However, the



603 introduction of BSG resulted in diminished properties, which could in part be counterbalanced  
604 by the addition of GTR. [122] [123]

605 Finally, Hejna et al. have studied in detail the impact of BSG as filler with various  
606 polymer matrixes (NFC, PCL), and the interactions with them. [124] [125] [126] They showed  
607 that the proteins contained in BSG improved the interfacial compatibility by participating in  
608 Maillard reactions to form melanoidins. Extrusion temperature was found to be the most  
609 determining factor for these reactions, more present at higher temperature (> 180°C), doubling  
610 the antioxidant power but bringing a strong brown colouration of the polymers. However,  
611 despite the good compatibility, BSG addition showed to be detrimental for mechanical and  
612 thermal performances. Furthermore, terpenes and terpenoids were liberated during the  
613 extrusion step that can be harmful for human health and the environment.

614 The use of BSG as filler could allow the valorisation of large amounts of this inexpensive  
615 and sustainable by-product of the agri-food industry but in reality, the percentage that can be  
616 introduced in polymer matrixes is limited to avoid impairing the thermo-mechanical  
617 performances and water resistance. A few examples with successful results were nonetheless  
618 listed, requiring improvements with coating or strengthening steps, to fully take advantage of  
619 the intrinsic antioxidant and antimicrobial properties of this functional filler. [120] These  
620 challenges will need to be addressed and compared to the results of other biomasses to  
621 understand better the potential of BSG as natural filler in composite materials.

## 622 **7 Challenges and future directions**

623 Several challenges and obstacles were outlined within this review that will need to be  
624 solved in the future for an optimal valorisation of this promising bioresource. Firstly, the use  
625 of dried BSG results in a significative carbon footprint (drying) and the use of the wet biomass  
626 would be preferable, while keeping in mind the perishability of the latter and the need for  
627 particle size reduction. New strategies, especially regarding the obtention of valuable building  
628 blocks and their transformation into biopolymers are required to diversify the options in terms  
629 of building blocks and platform molecules availability, as well as final polymer properties. The  
630 scale up of such chemical upcycling route has seen little interest this far but is paramount for  
631 the integration of such valorisation within biorefineries to facilitate higher value valorisation.  
632 The economic and environmental impact have started to be investigated, but more

633 comprehensive studies are still required to evaluate the economic impact of such valorisations  
634 for breweries, their economic feasibility in a context of biorefinery, the environmental impact  
635 through LCA for example, as well as the comparison of above-mentioned criteria with  
636 different biomass valorisations. For an application as natural filler, the introduction of BSG  
637 often proved to be detrimental for the final material and the development of new strategies  
638 are required. In conclusion, to valorise large amounts of BSG, a combination of both polymer  
639 and composite material approaches could be ideal. A part of BSG's lignocellulosic biomass  
640 could be fractionated and valorised as polymeric matrix of high-performance, non-toxic or  
641 ecotoxic, biodegradable polymers, to which the rest of the biomass could be added as  
642 renewable filler. This strategy could help upcycle this waste biomass in larger amounts while  
643 using BSG as a whole in a biorefinery strategy without compromising its potential properties  
644 (physicochemical and water resistance). Such biorefineries have to be modelised to help  
645 providing high value products while targeting carbon neutrality throughout the valorisation  
646 process.

## 647 **8 Conclusion**

648 This review gathers information on the possible ways to valorise Brewer's Spent Grain  
649 with an emphasis on building block obtention for polymer synthesis as well as its use as  
650 natural filler. The advantages of such a bioresource are its low price, high availability  
651 throughout the year and variable and tuneable composition of the fractions of interest  
652 depending on malt type. Finally, another advantage of BSG is its soft matrix found to be the  
653 easiest to fractionate compared to other biomasses: milder conditions and shorter reaction time  
654 are needed resulting in greener valorisation pathways. However, BSG is rapidly perishable  
655 due to its high MC, leading to an expensive drying step with high environmental impact. Also,  
656 its soft matrix leads to a higher sensitivity to degradation, especially for carbohydrates  
657 fractions that can be degraded in furan derivates and humines.

658 Conditions reported in the literature for the extraction and degradation of each fraction  
659 (hemicellulose, cellulose, lignin, protein) of BSG's lignocellulosic matrix were reviewed  
660 alongside full fractionation examples for BSG or similar biomasses. This shows that many  
661 different conditions can be used depending on the biorefinery strategy and the desired form  
662 of each fraction (polymeric, oligomeric, monomeric). However, the conditions used for each

663 step might have a significant impact on the subsequent conditions as it could alter the  
664 structural organisation of the remaining fractions. All available building blocks obtained from  
665 the extraction and degradation of BSG's fractions were described. Furthermore, their use as  
666 starting materials for useful monomer or polymer synthesis was discussed. Only a few  
667 examples of BSG's chemical valorisation for polymer applications have been presented so far,  
668 but the examples listed herein show great potential. BSG's use as natural filler was also  
669 reviewed but its introduction often resulted in inferior properties and performance as well as  
670 increased water sensibility. Post treatments helped to mitigate these properties drops but  
671 BSG's percentage was often limited to 10-20 wt% or even less.

672 Finally, the challenges and potential directions of investigation were discussed,  
673 reviewing the necessary steps towards a more efficient valorisation of this promising brewing  
674 by-product. A lot has yet to be achieved to this end, but the environmental, economic and  
675 societal output are driving forces considering the global amount produced as well as the  
676 current valorisation options available.

## 677 9 References

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679

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