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2 **Valorisation of Brewer's Spent Grain: Lignocellulosic**

3 **Fractionation and its Potential for Polymer and Composite**

4 **Material Applications**

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9 **Abstract:**

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

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

27 **1 Introduction**

28 In a context where our economical and consumption model is mainly designed to be linear,
29 the global annual production of wastes is estimated around 2 billion t/a, continuously growing to
30 reach the expected amount of 3.4 billion t/a by 2050. An evolution of the consumption and
31 production habits has recently been witnessed, supported by the scientific community through

32 the development of green chemistry for example, providing new and greener alternatives to meet
33 the demands of sustainable production. Plastic is one of the largest pollutants with a generation
34 of more than 350 million t/a waste globally, according to the OECD (Organisation for Economic
35 Cooperation and Development) with only 9-10% of material being recycled [1, 2]. Furthermore,
36 plastics are majorly petroleum based and non-biodegradable, leading to an accumulation of such
37 materials in the environment and a dependence on non-renewable resources, highlighting the
38 necessity for a more sustainable design for material production. To this end, the use of biomass
39 can be appealing to meet the challenges presented. In particular, the by-products of the agri-food
40 industry are often under-utilised or valorised for low-value products. The use of such waste
41 biomass has recently seen a growing interest, allowing to reduce the dependency on fossil
42 feedstocks while avoiding the stress on current crops or land for various fields of application:
43 activated carbon for dyes or pollutants adsorption from cilantro or waste tea [3, 4], spent coffee
44 grounds in composite materials [5], extraction of bioactive compounds from tomato pomace or
45 orange peels [6, 7]. In the field of materials, the conception of novel polymers with good
46 biodegradability profile, low toxicity and ecotoxicity, while using wastes as raw materials, is a
47 necessary step to drive this industry towards a more sustainable future. New synthetic and
48 production strategies are thus required to obtain new monomers to be used as building blocks for
49 polymers and composite materials. In this review, the focus will be placed on the valorisation of a
50 by-product from the brewing industry, Brewer's Spent Grain (BSG), a promising under-utilised
51 and undervalued renewable raw material. The valorisation of waste biomass as feedstock
52 described herein is in accordance with the 12th Sustainable Development Goal listed by the
53 Department of Economic and Social Affairs from the United Nations [8].

54 While the brewing activity was started approximately 6000 years ago by the Sumerians [9],
55 the global production of its major component: barley (*Hordeum vulgare L.*) reached 141 million
56 t/a in 2016 [10, 11], corresponding to an overall estimated beer production between 182 and 340
57 billion litres/a from 2016 to 2021 [12–14]. While the fermentable sugars (wort), extracted after
58 mashing and sparging, will be used for beer production through fermentation, the main by-
59 product of the brewing process is BSG (Brewer's Spent Grain). BSG represents 85% of the by-
60 products [1]; 100 kg of malt will produce 100-130 kg of BSG with a high moisture content (MC)
61 between 70-80%. The production of BSG is commonly estimated at 20 kg/100L of beer [15–17],
62 which represents a global production of 36.4-39 million t/a in 2019 [13–16, 18, 19], raising over
63 40 million t/a today and corresponds to a waste generation of 3.4 million t/a (2008) in Europe
64 alone [20].

65 BSG is an inexpensive raw material with an estimated cost around 35€/t of dry matter [18]
66 or 42 USD/t [21]. Its all-year-round availability and low cost make it an interesting resource for

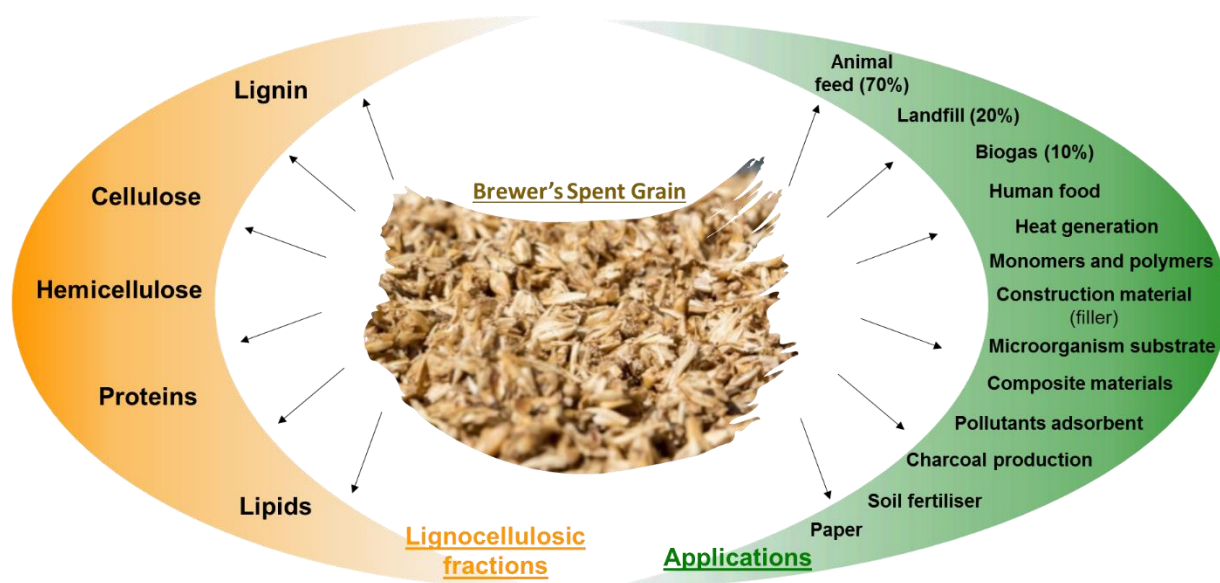
67 various applications. However, it is rapidly perishable due to microbiological instability: high MC
68 and presence of fermentable sugars, with a shelf life of 2-10 days depending on storage conditions
69 [22]. The major part of its cost is brought by the drying process of this biomass due to its high
70 moisture content [21] with a high environmental impact of 495-770 kg_{CO2}/t_{BSG} (CO₂ equivalents).
71 Arranz et al. have developed a solar oven as an alternative to conventional drying techniques for
72 BSG (convection drying [23] or infra-red drying [24]), lowering the environmental impact to 0
73 kg_{CO2}/t_{BSG} but increasing the drying time 10-fold [25]. The elimination of the water contained in
74 renewable biomass is a major challenge that needs to be taken into account when designing
75 valorisation routes to prevent having a greater environmental impact than the petroleum-based
76 counterpart they try to supplement. Examples of biomass valorisation have shown that water
77 elimination can cover up to 80% of the energy cost of a valorisation strategy [26]. Thus, an LCA
78 (Life Cycle Analysis) should be performed, when possible, to confirm the benefit of such routes
79 and new materials. By assessing the techno-economic feasibility, the environmental impacts and
80 energy consumption of BSG's valorisation, a recent study showed that water removal was indeed
81 an important step of the process in terms of environmental impact, advocating mechanical
82 dewatering such as screw, centrifugal, hydraulic or membrane filter presses. Without eliminating
83 the risk of microbial growth of BSG like a complete drying would, the mechanical dewatering
84 should prolongate the shelf-life of BSG before its valorisation, that can be as low as 48 hours for
85 wet BSG. Alternative drying methods such as microwave drying could eliminate water with a
86 limited CO₂ emission, reaching moisture levels below 10% [27].

87 Finally, the use of this massively produced bio-based waste that is BSG has attracted the
88 scientific community's interest only recently with a few publications per year in the 80's up to
89 around 330 annually more recently [28], still timid considering the volumes generated and the
90 valorisation options available to this date. In 2020, 70% of the BSG was valorised for animal feed,
91 10 % for the production of biogas, while 20% were eliminated in landfills [22]. This last option to
92 dispose of the BSG waste equates to an environmental impact of CO₂_{eqv}=513 kg/t_{BSG} [29]. It would
93 thus be important to valorise this resource more efficiently by producing higher value products
94 that would encourage breweries to further upcycle this resource.

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

102 BSG will be investigated, followed by their use for polymer synthesis. The use of BSG with limited
 103 transformation as renewable filler for composite material application will be described.

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



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

113 2 Composition

114 BSG's composition varies greatly depending on various parameters such as barley variety
 115 and type (grilled, roasted, according to beer type), kilning temperature (KT, drying of the green
 116 malt after germination), malting process, mashing conditions, to name but a few [11, 30]. As an
 117 example, the kilning temperature has a significant impact on the total phenolic content (TPC) of
 118 the malt with higher values (4 fold) [13, 31] recorded for paler malts with lower KT [10, 32]. The
 119 mashing conditions allow to reduce carbohydrate content from 65 to 49 % by extracting most of
 120 the fermentable sugars leaving cellulose and hemicellulose behind [20]. However, the remaining
 121 composition with high moisture content (75-80 %) is particularly vulnerable to bacteria, yeast
 122 and mould development [30]. The composition of lignocellulosic biomass (LCB) such as BSG is
 123 usually determined through fractionation and include cellulose, hemicellulose, lignin, protein,
 124 lipids and ashes [33], with a C:N ratio of 13.9 for BSG [34]. A meta-analysis of articles and reviews
 125 from the literature was conducted, gathering up to 38 references and the middle values alongside
 126 minimal and maximal percentage values are reported in Table 1 for BSG's composition

127 (percentage of dry matter) [13, 15, 21, 32, 35–41]. For each fraction of BSG’s lignocellulosic matrix,
 128 the percentage can go from simple to double, which confirms the high variability of its
 129 composition. However, it can be an advantage as the selection of a certain malt type and extraction
 130 conditions can yield to a tailored composition richer in one or several fractions of interest,
 131 improving the potential 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
Proteins	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 main
 135 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 arabinoxylenes (AX) with a xylose/arabinose ratio of 7:3, considered as rare sugars
 138 [15, 32, 36, 42–44]. The third fraction of BSG is proteins (15-25 %DM) [41], mainly composed of
 139 hordein, gluten, globulin and albumin [45], with a composition of amino acids that greatly varies
 140 between pale and dark malt [46]. Extracted proteins from BSG (104.2 mg/g_{BSG}) [47] can be
 141 degraded in enzymatic conditions (*Aspergillus niger*) yielding 17 amino acids with the most
 142 prominent being valine, alanine, phenylalanine, tryptophan and proline [48]. BSG is also
 143 composed of a non-negligible fraction of lignin, followed by a smaller amount of lipids with a fatty
 144 acid profile dominated by linoleic acid (47%) and palmitic acid (32%) [40]. BSG presents a high
 145 proportion of TPC (1735 $\mu\text{g/g}$), vitamins (64 $\mu\text{g/g}$), and minerals (8588 $\mu\text{g/g}$) [13], justifying the
 146 interest for its use in human and animal feed. However, a strategy that would allow the complete
 147 valorisation of this by-product for higher-value products while using the intrinsic
 148 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 overview of
 151 the alternative applications will be presented. Thanks to its interesting composition, rich in
 152 protein, minerals, vitamins and TPC, BSG is a by-product of the agrifood industry interesting for
 153 human food or animal feed [49]. However, the price of BSG has to be very low to match standard

154 prices for these applications which can be challenging when considering drying and transport
155 costs; alternative higher-value valorisation routes would be preferable [13].

156 • **Animal feed:** Wastes from the agrifood industry only represent 5 % of the animal feed market
157 but the use of BSG for such an application allow the valorisation of considerable volumes of
158 this by-product from the brewing industry. Its use (20-30 wt% dry matter) for cattle has shown
159 significant improvement in milk yield but requires the use of additives to prevent
160 contamination and improve preservation [50].

161 • **Human food:** Despite the variation of its composition, BSG always contains high amount of
162 fibres, proteins, minerals, antioxidants, lipids and vitamins useful for human consumption [51].
163 BSG can be crushed and mixed by extrusion to prepare flour [52], for fibre and protein-
164 enriched pastas [53], added in biscuits, bread, etc [54]. Cookies baking using fresh BSG is a
165 popular valorisation of this by-product amongst home brewers [9]. Protein hydrolysate have
166 displayed antioxidant and anti-inflammatory activities and could be used as bioactive edibles
167 [45]. Nyhan et al. recently reviewed the advantages of BSG (high fibre and bioactive content)
168 for human nutrition and its potential to equilibrate diets to prevent diet-related diseases, as
169 well as tackling undernourishment in developing countries thanks to its high availability and
170 low cost. On the environmental point of view, BSG's derived food was found to exhibit lower
171 global warming impact (CO₂ eq), land use, fresh water and marine eutrophication than other
172 biomasses (soybean, pea, whey) [55].

173 • **Heat generation:** The most efficient way to use BSG for combustion application is under pellet
174 form and could be used directly as fuel for heat production in microbreweries [56]. Its calorific
175 value equals 9.6-11.3 MJ/kg, similar compared to other biofuels for combustion [23]. However,
176 this requires a costly preliminary drying step and its combustion liberates particles and toxic
177 gases: NO_x and SO_x, 480 and 1000-3000 mg/m³ respectively [23, 43]. Recently, a hydrochar
178 from BSG was prepared through microwave-assisted hydrothermal carbonisation, reported
179 with a high calorific value: 32 MJ/kg [57], alongside a bio-oil fraction (26 MJ/kg) and a
180 saccharide-rich aqueous fraction [58].

181 • **Other applications:** The valorisation of BSG for the production of biodiesel, biogas, bioethanol,
182 biohydrogen or biobutanol has recently attracted the interest of the scientific community [56].
183 Otherwise, its carbonisation followed by an activation allows the production of activated
184 charcoal. Other reported usage of BSG mention paper production, as adsorbent for pollutant
185 and dyes elimination in water, substrate for microorganism and yeast, fungi growth or as soil
186 fertilisers [44, 58].

187 Finally, BSG can be chemically valorised into higher-value building blocks to be used as
188 monomers for polymer or organic compounds synthesis. The focus of this review will be on the

189 obtention of such building blocks as well as their use in polymer chemistry. Additionally, BSG can
190 be used as natural filler for composite material applications when mixed with polymer matrixes.

191 **4 Biomass fractionation**

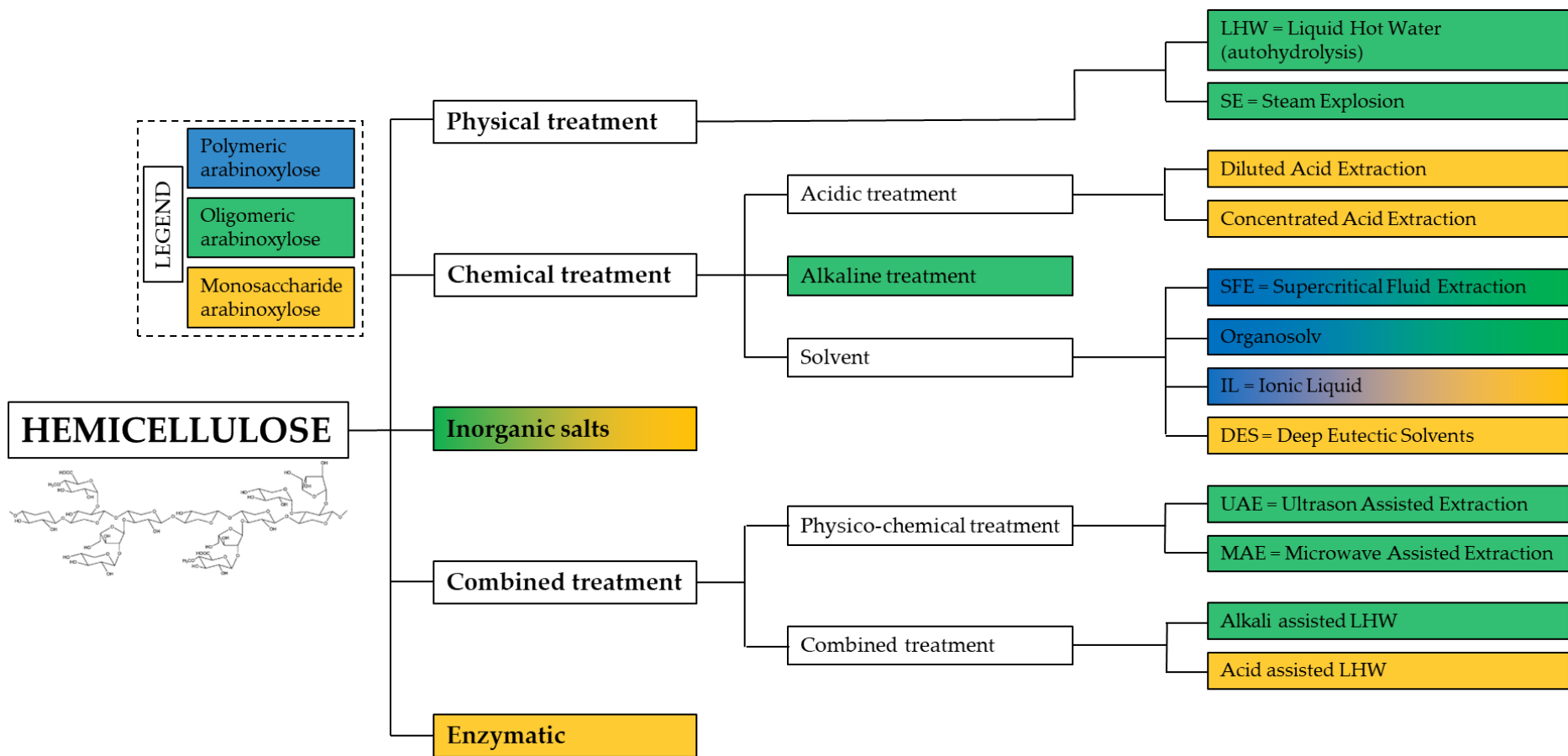
192 Lignocellulosic biomasses (LCB) are appealing raw materials than can yield various
193 amounts of hemicellulose, cellulose, lignin or protein but their fractionation into compounds of
194 interest can be challenging, due to the strong entanglement of those fractions. More specifically,
195 cellulose shows a higher resistance to extraction and degradation (hydrolysis) treatments due to
196 its crystalline/semi-crystalline nature. Table 1 gathers the compositions of 38 references showing
197 middle values and percentage ranges of BSG composition (dry matter). Unlike some of the other
198 renewable lignocellulosic materials, the production of BSG is not in competition with the food
199 sector as it is a waste from the agri-food industry [59]. Furthermore, its lower matrix density
200 allows for more efficient extractions in milder conditions.

201 LCB fractionation has been widely studied using various strategies depending on the
202 starting material and targeted fraction but still represents an important challenge for an efficient
203 valorisation of biomass and the development of biorefineries. After reviewing the available
204 conditions for the extraction and degradation of each fraction of the lignocellulosic matrix,
205 examples of biomass full fractionation will be presented in section 4.6, focusing on BSG biomass
206 or similar ones such as wheat straw. A stronger focus will be placed on the treatment of
207 hemicellulose due to its easier extraction thanks to the easily extractable and degradable
208 amorphous nature of this polymer, yielding interesting building blocks [44].

209 **4.1 Hemicellulose extraction**

210 Hemicellulose extraction has been extensively investigated throughout the fractionation of
211 various LCB and available conditions for BSG or similar biomasses are summed up within Figure
212 2 alongside a brief description of their advantages and disadvantages listed in Table 2. These
213 processes include liquid hot water (LHW) also called autohydrolysis, steam explosion (SE),
214 alkaline treatment, organosolv, ionic liquids (IL), deep eutectic solvents (DES), supercritical fluids
215 (SFE), enzymatic extraction, ultrasonic- and microwave- assisted extraction (UAE and MAE) and
216 finally diluted and concentrated acidic treatment (DAE and CAE respectively). The mechanisms of
217 hemicellulose breakdown have been investigated by Lu et al. [60] but most of the conditions only
218 extract hemicellulose under polymeric form or slightly degraded to oligomers or suffer from
219 toxicity and yields limitations for example. The last two treatments presented (acidic conditions)
220 are known to be the most efficient for the complete breakdown of the hemicellulose to the
221 monosaccharides units which is more interesting to obtain building blocks for polymer synthesis
222 purposes and will thus be studied in more detail 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 the
225 potential of xylo-oligosaccharides (XOS), ideally recovered after LHM pre-treatment of LCB
226 (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 [61].



230

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

232

233

234

235

236 **Table 2** Summary of available hemicellulose extraction processes alongside their advantages and disadvantages.

Treatment	References	Arabinoxyllose form	Selectivity and efficacy
LHW	[60, 62, 63]	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	[62, 64]	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	[44, 60, 62, 64-71]	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	[44, 60, 62, 64-70]	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.
Alkaline	[60, 72]	Oligomeric: 49200-64300 g/mol	Saponification at 80-150 °C between ferulic acid from lignin and AX, liberating hemicellulose in high yields.
SFE	[9, 60, 73]	Polymeric/ oligomeric	70-80% Yield but with high amount of degraded products (like humines) using supercritical CO ₂ (40°C, 175 bar) or subcritical water (200-260°C). Possible to obtain aromatic moieties through hydrothermal carbonisation.
Organosolv	[60]	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.
IL	[62, 74]	Polymeric/ monosaccharide	[Amin]Cl used to break H-bonding and liberate AX (75 % yield) under polymeric form except for [C ₂ mim][OAc] liberating monosaccharides. Difficult to separate products and IL to regenerate them.
DES	[28, 60]	Monosaccharide	ChCl/Glycerol DES exhibit low selectivity: degradation of cellulose. Replacing glycerol by lactic acid or urea allows to separate the extracted cellulose.

UAE	[60, 75–77]	Polymeric/ oligomeric	Combination with alkaline conditions to obtain oligomers, polymers or fermentable sugars for bioethanol production (75 % AX yield on oat).
MAE	[60, 78]	Oligomeric	More efficient extraction than UAE: 1-5 min vs 10-30 min for UAE (77 % yield).
Inorganic salts	[62]	Oligomeric	Alternatives to acidic hydrolysis with less corrosion and recyclability issues using NaCl, KCl, CaCl ₂ , MgCl ₂ , FeCl ₂ , ZnCl ₂ , FeSO ₄ , FeCl₃ (89 % yield).
Enzymatic	[70, 79]	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. [2]

237

238 **4.2 Saccharification of BSG (hemicellulose acidic treatment)**

239 Diluted and concentrated acidic extraction (DAE and CAE respectively) allow the
240 breakdown of hemicellulose into monosaccharide. Even though stronger acidic conditions
241 improve the homogeneity of the reaction and allow the use of lower temperature and pressure
242 [44], it faces corrosion, acidic waste management and stronger degradation issues converting
243 sugars into furanic moieties or humines [66]. Even though this decomposition can be slowed by
244 adding protectors such as ethyl-ethyl ketone [44], these conditions are typically used for the more
245 robust crystalline carbohydrate polymer, cellulose, to produce glucose using 10-30 % H₂SO₄ for
246 example. These conditions can even be used to directly produce furanic derivatives and optimised
247 using MAE or UAE [44].

248 A wide range of acids have been investigated to hydrolyse hemicellulose and are listed in
249 Table 3 alongside their specificities and advantages [44, 60, 62, 63, 80]. Overall, sulfuric acid is
250 found to be the most efficient and selective catalyst for acidic hydrolysis with the highest
251 monomeric xylose and arabinose yields while leaving the cellulose in the solid fraction [62]. The
252 combined severity (CS) evaluates the severity of a treatment using time, pH and temperature.
253 Highest xylose yields are obtained for low severity (CS<2-3) while higher values increase
254 saccharides degradation into furanic compounds (furfural for pentose and 5-HMF for hexose),
255 confirming the use of DAE for optimal saccharification. Even higher CS will dehydrate
256 carbohydrates further to form pseudo-lignin increasing the amount of Klason's Lignin [66].

257 **Table 3** List and advantages of acids used for the extraction and saccharification of BSG's hemicellulose.

Acid	Specificity and advantages
H₂SO₄	Best reactivity and selectivity
HCl	Reactivity similar to sulfuric acid but lower selectivity (glucan dissolution): preferred for cellulose degradation
HNO₃	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 %)
p-Toluene sulfonic	Increased solubility
Super acids	C-SO ₃ OH (carbon-based solid acid): allows the use of reduced temperature, water usage and corrosion issues
Phosphoric	-
Formic	-

258 To better understand the hydrolysis of polysaccharides into monosaccharides, Mäki-Arvela
259 et al. [44] have studied its kinetics and mechanisms to optimise reaction conditions for improved

260 yields and reduced amounts of degradation products (furans and humines). The mechanism is
261 either based on the protonation of glycolic bond or the pyranic oxygen and the kinetics are
262 dictated by their structures with β -anomers showing weaker tension, such as arabinose.
263 Reactivity can thus be ordered increasingly as such: glucoside < mannoside < galactoside <
264 xyloside < arabinoside, in accordance with the selectivity observed with diluted oxalic acid
265 hydrolysis (Table 3). However, a higher reactivity also implies higher risk of degradation along
266 the following chain: xylan \rightarrow xylose (oligomeric) \rightarrow xylose (monomeric) \rightarrow furfural \rightarrow humines
267 [65], as well as the formation of side products such as levulinic and formic acids, justifying the use
268 of low amount of acidic catalyst [44].

269 One advantage of BSG compared to other LCB, apart from its high availability and low price,
270 is the composition of its hemicellulose exclusively made of rare sugars [44]: xylose and arabinose
271 with a 7:3 ratio, similar to wheat straw. Its main advantage is the lower density of its matrix,
272 making its hemicellulose extraction easier and more efficient: 37 minutes for BSG against 12 hours
273 for hard wood in similar conditions. This increased reactivity is due to the lower apparent
274 activation energy of agri-food wastes estimated at 50 kJ/mol (wheat straw) against 100-200
275 kJ/mol for wood derivatives, resulting in lower operating temperatures: 100-200°C against 150-
276 250°C. However, this increased reactivity can lead to stronger degradation into furan derivatives
277 when comparing corn and pine biomass for example which require the need of milder reaction
278 conditions [44]. It is noteworthy to mention that the use of continuous flow saccharification
279 developed by Harris et al. allows to avoid the degradation of the monomeric sugars [81]. In the
280 end, BSG was found to be the most interesting raw material for lignocellulosic fractionation and
281 hemicellulose hydrolysis when comparing various biomasses (hard wood, soft wood and several
282 agricultural wastes), with a xylose yield around 95 % (similar to wheat straw) and requiring the
283 lowest temperature and reaction time [44]. Finally, the extracted sugars can be separated, after
284 filtration of the salts from the acid catalyst, using ionic exchanger resins for example [44], but it is
285 best to use the mixture of sugars if possible, to reduce the number of steps and environmental
286 impact of purification and separation procedures. The use of BSG as bioresource for the obtention
287 of hemicellulose or monosaccharides is thus competitive compared to other biomasses, allowing
288 higher yields and the use of milder reaction conditions and shorter reaction time, leading to
289 greener processes.

290 **4.3 Protein extraction**

291 The protein fraction in LCB is usually easy to extract, especially for BSG that has a softer
292 matrix. An example of mild conditions is described by Connolly et al. where BSG was put in the
293 presence of water at 60°C for 18 hours before centrifugation and precipitation at -20°C [46]. One
294 of the interesting findings is the nature of the proteins with larger profile for pale BSG (59 % > 10

295 kDa) compared to black BSG (6 % > 10 kDa) and a high antioxidant profile thanks to a high TPC.
296 Vieira et al. used a more sequential approach for protein and arabinoxylan extraction under basic
297 conditions. Each hemicellulose extract was acidified using citric acid (pH = 3) precipitating the
298 proteins, recovered by filtration. The acid was then recovered by precipitation in ethanol to yield
299 oligomeric arabinoxylane [82]. Optimised extraction conditions were investigated using UAE
300 yielding high amount of proteins from BSG (104.2 mg/g_{BSG}) [47] and subsequently 17 amino acids
301 after enzymatic lyse [48]. Du et al. reviewed protein extraction conditions on different biomasses
302 including BSG and cyanobacteria (*Arthrospira platensis*, AP) [83]. Three conditions were
303 investigated with the LHW as standard, alkaline treatment as milder conditions (40°C) and
304 subcritical method (200°C, 40 bar) as greener method with an extraction time of 20 minutes but
305 at an increased cost. The highest protein extraction yield was obtained with alkaline treatment:
306 21.4 wt% for BSG and 55.5 wt% for AP with purities of 60.2 and 68.8 wt% respectively with the
307 rest of the extract being mainly composed of oligomeric hemicellulose or traces of cellulose.
308 Proteins can also be extracted with similar efficiency in acidic conditions as described by Babu et
309 al [84]. Another approach by Sajib et al. or Niemi et al. is to remove the hemicellulose fraction
310 enzymatically in order to extract proteins from BSG without saccharides in alkaline conditions
311 [38, 79]. The simultaneous recovery of proteins and carbohydrates is also possible by using a
312 mixture of carbohydrase and peptidase yielding hydrolysates to be used as prebiotic food
313 supplement for example [85].

314 As explained previously, the reported use of BSG is almost systematically performed on dry
315 BSG for transportation and preservation purposes mainly, but this drying step comes with a non-
316 negligible environmental cost [25]. Tackling this issue, Connolly et al. proposed a more
317 sustainable valorisation using wet BSG yielding protein-rich hydrolysate (< 5 kDa), with a
318 different amino acid composition reported between pale and dark malt. To overcome the non-
319 grinded nature of wet BSG, compared to the dry one that is easily shredded, the stirring was
320 performed by an Ultra Turrax, to reduce particles size while keeping a good homogeneity [46].

321 To summarise, protein extraction can be achieved easily using several methods. However,
322 if the high amount of protein is the fraction of interest for food application, the other fractions
323 (fibres, vitamin, minerals) comprised in BSG could be of interest [45, 50, 51]. Other possible
324 applications for this protein fraction or hydrolysate lies in the cosmetic sector where such
325 compounds from wheat and oat are already used for their moisturizing and nutritive properties
326 [86]. Protein extract could also be used for edible film production out of prolamin, or for
327 composite materials using BSG's hordein [27].

328 **4.4 Lignin extraction**

329 The high content in phenolic compounds from the lignin fraction could be interesting for
330 the design of active packaging through intrinsic antioxidant properties or to mitigate the effect of

331 oxidative stress in nutraceuticals, cosmetic or medical application (anti-inflammatory, anti-
332 atherogenic, anti-cancerous) [87]. Standard measurement of TPC (Folin-Ciocalteu reagent) gives
333 TPC values of 3-4.7mg_{gal}/g_{BSG} (gallic acid equivalent) [31, 88] and phenolic compounds
334 (hydroxycinnamic acids), corresponding to 1-2 wt% of BSG, are mainly represented by ferulic acid
335 [39]. These hydroxycinnamic acids are usually extracted through hydrolysis in basic conditions
336 [89], whereas the best results were reported using enzymatic lyse yielding 4.61 mg/g_{BSG} [79, 90].
337 Even though UAE extraction does not improve extraction yields [31], an increase in temperature
338 (>160 °C) yields higher extraction efficacy which increases the antioxidant activity [91].

339 As lignin is a tough fraction of the LCB, often intertwined with the cellulose fraction, it is
340 often extracted in the later stages of the fractionation process. A standard way to recover lignin is
341 its extraction in basic conditions followed by a reacidification to force its precipitation. This
342 method is used by Mussatto et al. with a soda pulping process on BSG followed by the addition of
343 sulfuric acid in the black liquor. Different pH conditions were experimented with the best
344 conditions yielding 81 % of the solubilised lignin [92]. Using a different strategy, Niemi et al.
345 described an optimised protocol in 3 steps with first, the enzymatic degradation of carbohydrates,
346 then the enzymatic lyse of proteins, followed by their precipitation in HCl, yielding a solution rich
347 in lipids and lignin under the degraded form of lignan [38]. Cassoni et al. investigated the use of
348 DES for lignin extraction from BSG and olive tree pruning (OTP), with a higher antioxidant power
349 reported for the latter. Good lignin yields (54.5 % for BSG and 37.8 % for OTP) were obtained with
350 purities over 75 % and similar M_w using a lactic acid (LA) and choline chloride (CC) (5:1) mixture
351 as DES for the delignification process [93]. Gbenebor et al. used diethyl ether to remove
352 extractable, before degrading carbohydrates (cellulose and hemicellulose) in strong acidic
353 conditions (10 M of H₂SO₄, HCl or acetic acid) then 5M NaOH and filtration, with the highest purity
354 (98 % purity) and yields (82.9 % of the lignin contained in BSG, representing 5.6 wt% of the
355 original composition) obtained when using H₂SO₄ [94]. Characterisation of the extracted lignin
356 showed good thermal stability with a T_g of 107 °C (H₂SO₄). Finally, organosolv treatment is a
357 possible procedure to recover the degraded lignin within a black liquor. This was described by
358 Parchami et al. after an acidic pre-treatment to eliminate the glucan-rich fraction [95]. The
359 organosolv process conditions were optimised using 50 % v/v ethanol to obtain precipitated
360 lignin with a 58 % yield and a 95 % purity.

361 Thus, lignin is a fraction more difficult to extract with multiple steps necessary. In addition
362 to its difficult extraction or dissolution, the presence of its aromatic components showed
363 inhibition for the enzymatic transformation of xylose to xylitol [44]. Furthermore, BSG is not the
364 optimal biomass to be selected if the fraction of interest is lignin, as barley shows a significantly
365 lower lignan content compared to other cereals such as rye or wheat [96]. Finally, the use of lignin

366 or building blocks from lignin for polymer synthesis usually yield higher resistance materials
367 thanks to its aromatic backbone but these materials show lower biodegradability profile
368 compared to other biopolymers from carbohydrates for example [27].

369 **4.5 Cellulose extraction**

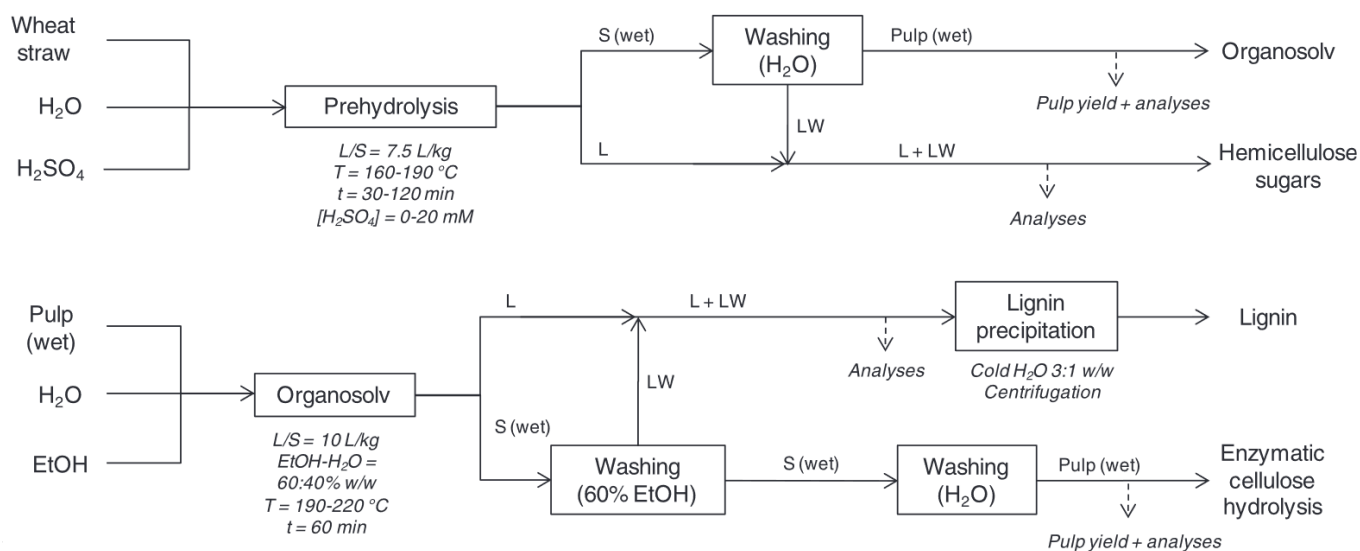
370 Few examples of cellulose extraction and valorisation from BSG are found in the literature
371 due the more complex accessibility, especially opposed to BSG's hemicellulose, being the most
372 easily extractable compared to other biomasses, and simple to convert to monomers. Matebie et
373 al. used a conventional approach for the obtention of cellulose with 3 pre-treatments to remove
374 hemicellulose and lignin: diluted acid hydrolysis, alkaline treatment, and bleaching [97]. The
375 obtained cellulose was then converted into CNC (Cellulose NanoCrystals) using concentrated acid
376 hydrolysis (51 wt% H₂SO₄). The synthesis parameters were optimised to yield cellulose with
377 43.24 % and a high crystallinity.

378 Mäki-Arvela et al. reviewed the conditions reported for the extraction and hydrolysis of
379 cellulose. Due to its resilience, most available methods suffer from drawbacks such as corrosion
380 and waste management issues for strong acids or the need of high temperatures for mild acids,
381 both leading to significant dehydration of sugars, whereas the use of mineral acids generates large
382 amounts of salts after the neutralisation steps. Physical (ball milling, grinding, steaming) or
383 chemical treatments (SFE) can be applied to soften the crystalline structure (rated as CrI for
384 Crystallinity Index) to amorphous cellulose, to reduce its resilience. An alternative method to
385 produce glucose from cellulose are the vapours of HCl at 0°C [44]. One of the most efficient way to
386 valorise cellulose is through enzymatic hydrolysis, in comparison with hemicellulose that can be
387 degraded with simpler conditions and where microorganisms inhibitors (from lignin) are still
388 present lowering the lyse efficiency [44]. With a similar approach than Lynch et al. [70] with the
389 saccharification of the carbohydrate fractions from BSG using a cocktail of enzymes, Maache-
390 Rezzoug et al. focused more on the degradation of cellulose into glucose (48 g/100 g_{BSG}) alongside
391 arabinose and xylose production (5 and 9 g/100 g_{BSG} respectively). They used Cellulast, a mixture
392 of 4 types of enzymes to saccharify cellulose, after an instantaneous controlled pressure drop
393 process (DIC, an optimised SE) pre-treatment [97]. Similarly, Mishra et al. pre-treated BSG in
394 alkaline conditions before bleaching to produce cellulose nanofibrils (CNF), showing lower
395 crystallinity than the CNC described above [98].

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

400 4.6 Biomass full fractionation

401 LCB fractionation has been widely studied using several strategies depending on the type of
 402 biomass used and the fraction of interest, but for optimal comparability, only BSG or similar
 403 biomass (wheat straw or corn stalk) will be considered. As detailed previously (4.1),
 404 hemicellulose is easily separated by mild pre-treatments thanks to its amorphous nature which
 405 liberates and exposes lignin and cellulose that require stronger conditions to be separated and/or
 406 degraded. Like for BSG's dewatering, the use of mechanical treatment is preferred to soften the
 407 matrix, reducing the environmental impact of such fractionation [99]. One example of full
 408 fractionation of wheat straw biomass was described by Huijgen et al. and is shown in (Figure 3)
 409 [65]. A diluted acid extraction (DAE) pre-hydrolysis was performed to isolate hemicellulose
 410 selectively. After its removal, the rest of the matrix was subject to organosolv procedure to
 411 separate lignin and recover cellulose. For the latter, it was hydrolysed using enzymes to break it
 412 down to saccharides. The economic feasibility of such a biorefinery has been studied and would
 413 yield hemicellulose with an estimated price of 0.05 €/kg.



4

415 **Figure 3** Lignocellulosic biomass fractionation flow chart (wheat straw) described by Huijgen et al. [65] to
 416 separate hemicellulose, lignin and cellulose. Reprinted from W.J.J. Huijgen, A.T. Smit, P.J. de Wild, H. den Uil,
 417 *Fractionation of wheat straw by prehydrolysis, organosolv delignification and enzymatic hydrolysis for*
 418 *production of sugars and lignin, 2012, with permission from Elsevier.*

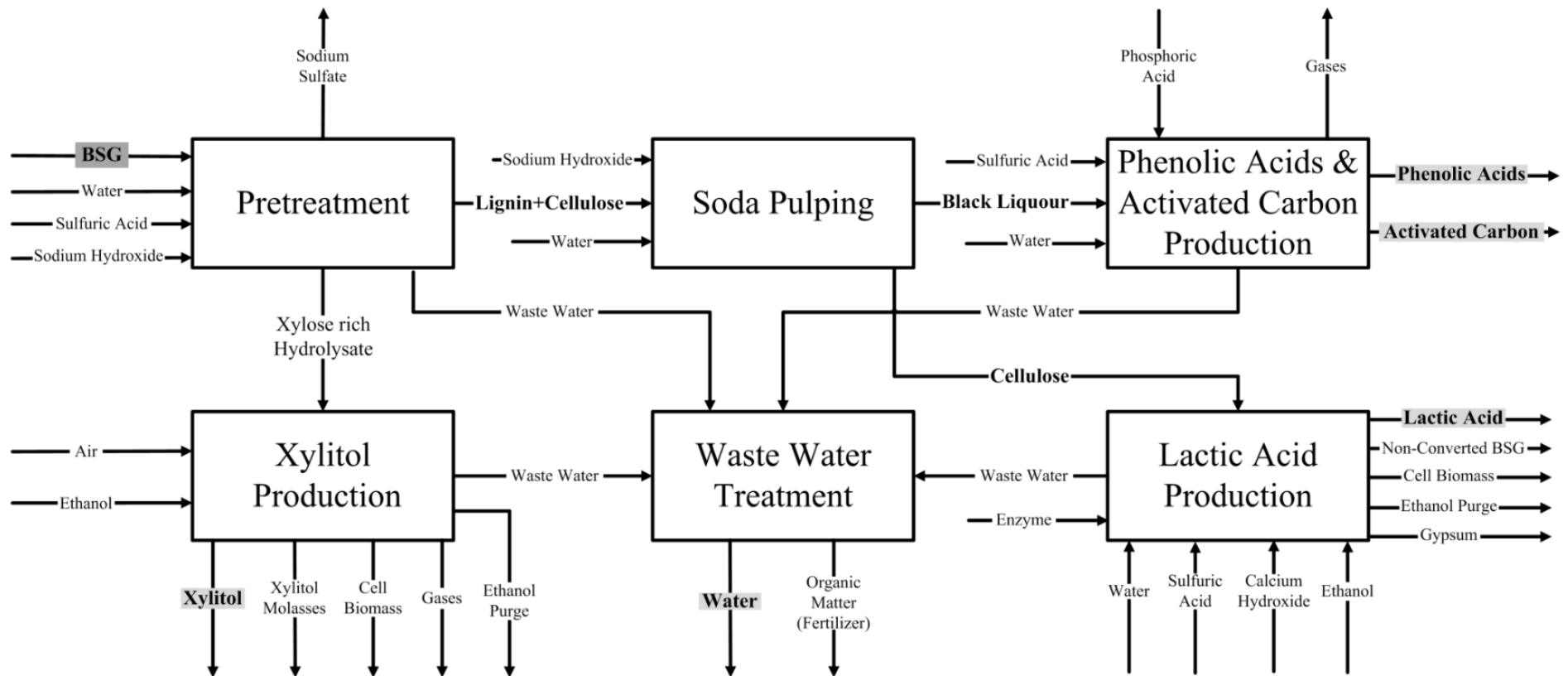
419 When studying the fractionation of corn stalk biomass, Zhang et al. have shown that the
 420 separation of lignin and cellulose (UAE in ethanol in their case) was strongly impacted by the
 421 pretreatment method used for hemicellulose extraction [100]. Indeed, after the LHW
 422 pretreatment, an alteration of the lignin matrix resulted in its repolymerisation during the cooling
 423 step, forming films around the cellulose fibers rendering their separation more difficult. The shift
 424 to a DAE or organosolv pretreatment to recover hemicellulose solved this issue [100]. To ease this
 425 tedious separation between lignin and cellulose, HIUS (high intensity sonication) softened the

426 matrix for a more efficient liberation of cellulose [101]. A larger-scale (1 ton) fractionation of BSG
427 was reported by de Crane d'Heyselaer et al. [102] to produce cellulose and lignin biopolymers in
428 a 3-step process with respective yields of 50.1 and 41.8 %. These polymers could in turn be further
429 degraded into building blocks of interest for packaging application through film forming for
430 example.

431 From all the condition reviewed for each fraction and examples of full fractionations of LCB
432 described, it can be concluded that various approaches are available depending on the biomass
433 used (milder conditions required for BSG for example) and the targeted form of the fraction
434 (polymeric, oligomeric, monomeric). Furthermore, the conditions used for each step might
435 significantly influence the following extraction conditions efficiency. When selecting the process
436 conditions for each step of the fractionation, it is important to keep in sight the form of the fraction
437 that is desired as well as the potential degradation of each component, especially for
438 carbohydrates that can be converted into furanic derivates or humines.

439 **5 Building blocks from BSG**

440 Few examples of chemical valorisation of BSG are reported in the literature with a full
441 fractionation of BSG to obtain various building blocks of interest, as developed by Mussatto et al.
442 and described below [21, 103]. As displayed in Figure 4, a DAE was used as an efficient mild pre-
443 treatment using citric acid to extract 91.8 % of hemicellulose under monosaccharide form,
444 yielding a xylose-rich hydrolysate. This fraction was in turn converted to xylitol with a 97.8 %
445 yield, while the rest of the LCB was treated in alkaline solution for delignification, yielding
446 phenolic acids and activated carbon after phosphoric acid activation and carbonisation [21]. The
447 cellulose-containing solid fraction was fermented using *Lactobacillus delbrueckii* to transform 99
448 wt% of the glucose into lactic acid (LA) after adjusting the pH for optimal yield [103]. The
449 economic feasibility of this strategy was validated by the biorefinery modelisation giving an
450 economical margin of 62.25 % with a PEI (Potential Environmental Impact) of the process of 0.012
451 PEI/kg and a carbon footprint of 0.96 kg CO₂-e/kg of BSG [21]. This shows the potential of BSG as
452 LCB to be chemically valorised, especially for polymer chemistry where these building blocks
453 could be of high interest.



454

455 **Figure 4** Full fractionation flowchart of BSG yielding various building blocks proposed by Mussatto et al. [21] Reprinted from S. I. Mussatto, J. Moncada, I. C. Roberto, C.

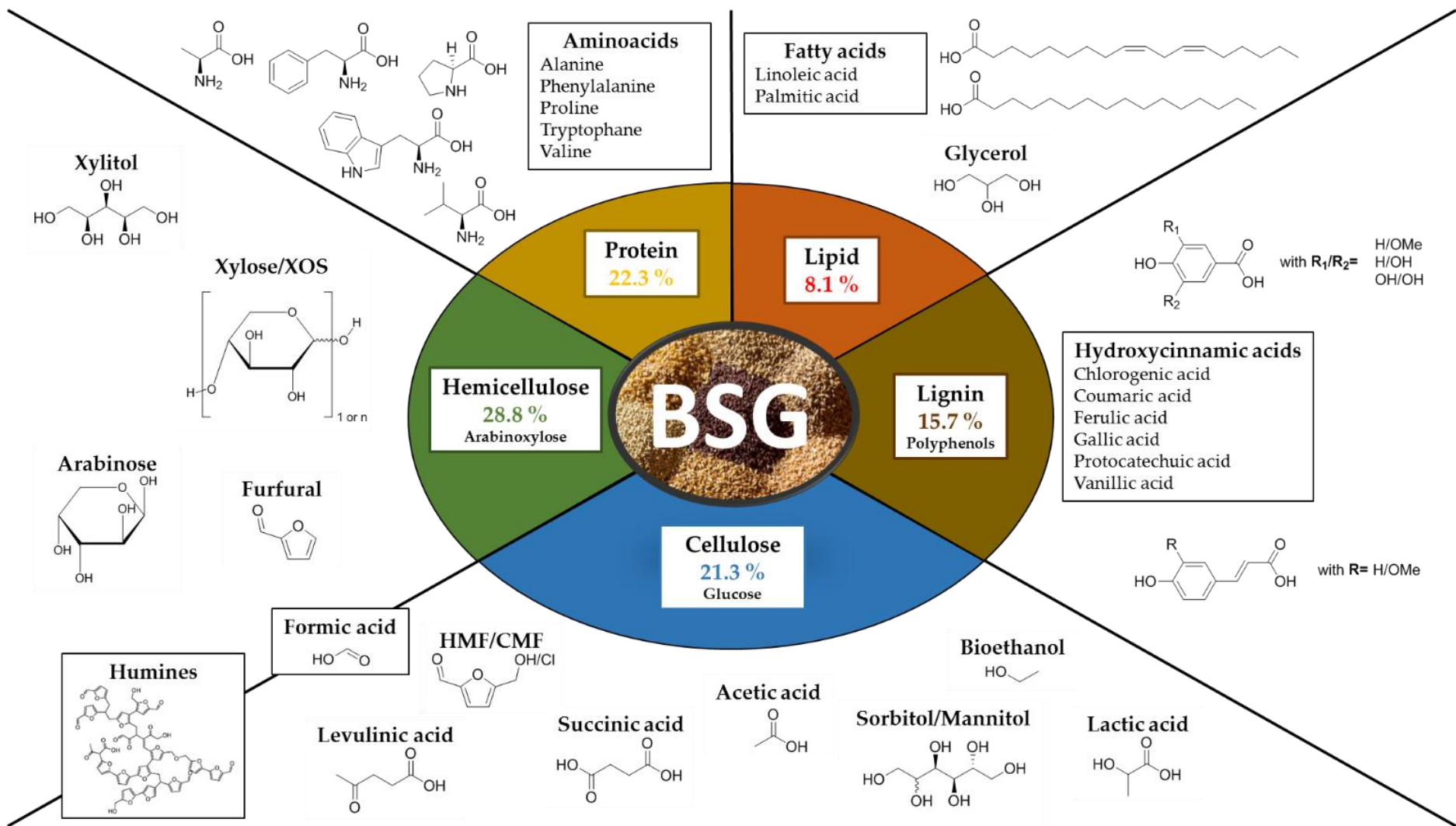
456 A. Cardona, *Techno-economic analysis for brewer's spent grains use on a biorefinery concept: The Brazilian case, 2013*, with permission from Elsevier.

457 The extraction and degradation of hemicellulose offers the possibility to obtain various
458 compounds of interest. Swart described an optimised pretreatment between the LHW and SE,
459 namely hydrothermal treatment (HTT), allowing the use of lower operating temperature and
460 dilution to obtain either xylose oligosaccharides (XOS) with a yield of 76.4 % or xylose from BSG's
461 hemicellulose [99]. Xylose could in turn be transformed into xylitol through catalytic
462 hydrogenation or microbial conversion, to be used for anti-inflammatory, anticaries or
463 sweetening applications. Otherwise, xylose can directly be degraded into furfural and ultimately
464 into formic acid [44].

465 The cellulose fraction can be degraded through glucose into a myriad of molecules such as
466 sorbitol and mannitol, obtained by heterogeneous catalysis with Ni or Ru or through
467 hydrogenation of cellulose. These could be used as sweetener, for vitamin C synthesis, or
468 converted to isosorbide, sorbitan, glycols, glycerol, lactic acid or sorbose. Alternatively, the
469 glucose obtained from cellulose could be converted into HMF or CMF and then into formic and
470 levulinic acid [44]. Another reported obtention of building blocks from BSG's cellulose was given
471 by Akermann et al. with an optimised fermentation using *Cellulomonas uda* to produce a mixture
472 of succinate, lactate and formate in small quantities (< 5 g/L) alongside larger quantities of
473 ethanol and acetate (> 25 g/L) with a global liquid product yield of 0.41 g_{prod}/g_{BSG}. The ethanol to
474 acetate ratio could be increased significantly by adapting the pH [104].

475 The overview of building blocks obtainable from BSG's lignocellulosic biomass (LCB)
476 according to the literature so far are displayed in Figure 5. The other minor fractions could lead
477 to phenolic acids from lignin, hydroxycinnamic acids more specifically, fatty acids and glycerol
478 from the lipid fraction and various amino acids from the protein fraction. A few techno-economic
479 analyses have assessed the feasibility for several building blocks (xylitol, protein, lactic acid) or
480 biopolymers productions showing the competitiveness of BSG's valorisation thanks to the low price
481 of the biomass and softness of its matrix, allowing simpler fractionation procedures and
482 functionalisation [21, 27, 105]. Some of the building blocks described here can be viewed as
483 platform molecules, allowing the obtention of a wider range of components. More specifically,
484 furan derivatives obtained from the hemicellulose and cellulose fractions are known to be
485 promising platform molecules thanks to their well-documented and efficient production from
486 carbohydrate and versatility of compounds obtainable through simple chemical transformations.
487 Compounds of interest obtained from furfural and hydroxymethyl furfural (HMF) are furan-2,5-
488 dicarboxylic acid (FDCA), diformyl furan (DFF), 5,5'-oxy-bis(methylene)-bis-2-furfural (OBMF)
489 [106], 2,5-bis(hydroxymethyl)furan (BHMF) to name but the most prominent ones, as well as
490 various linear diacids, diols and amine derivatives [107, 108]. These molecules are of high interest
491 for solvent, fuel [107], drug synthesis, surfactant synthesis [109] applications as well as

492 monomers for polymer synthesis [110, 111], with FDCA being one of the 12 most promising
493 building blocks for green chemistry.



494

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

496 Promising examples of BSG biomass fractionation have been described, showing the
497 potential of such an application for high valorisation strategies. However, challenges are still to be
498 overcome for an optimal valorisation such as efficient scale-up and biorefinery designing, to
499 assess the feasibility of complete valorisation of this bioresource, its economic viability and
500 environmental impact. Ideally, these chemical routes would use the wet biomass to limit the
501 environmental impact. These challenges will have to be addressed in the future to improve the
502 use of BSG and should be compared to other similar biomasses using comprehensive tools such
503 as LCA (life cycle analysis) (see section 8).

504 **6 Polymers and composite materials from BSG**

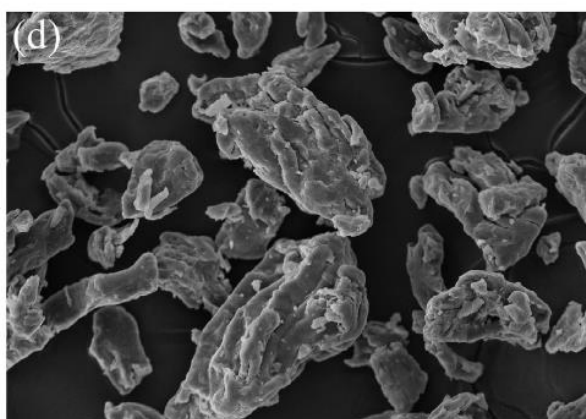
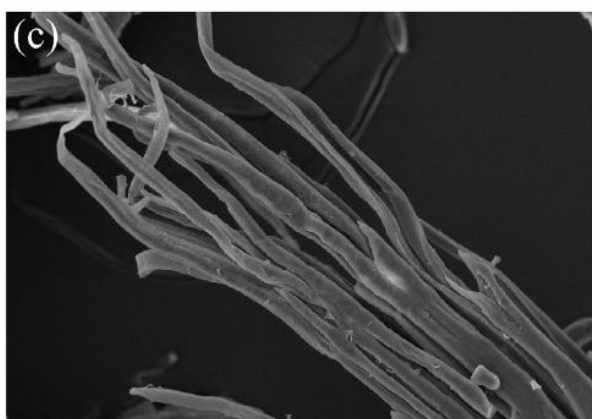
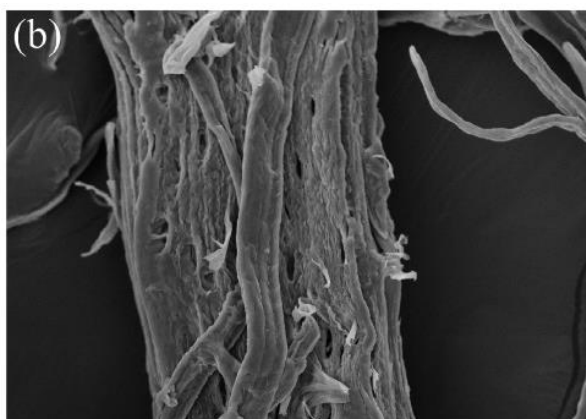
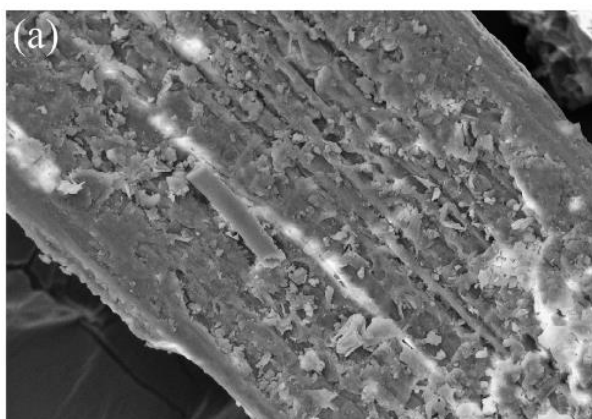
505 The synthesis of polymers can be an efficient way to valorise large quantities of BSG or any
506 biomass waste or by-product when it can be converted into interesting monomers or oligomers
507 building blocks. In turn, such polymeric materials could be produced in vast amounts, increasing
508 the use of renewable resources and potentially reducing low-value valorisation applications or
509 landfill of BSG. However, the improvement of the impact of such valorisation strategies should, if
510 possible, be assessed thoroughly with appropriate tools such as LCA [13]. At the core of the design
511 of these valorisation strategies should be included as much parameters as possible for optimal
512 reduction of the environmental footprint: impact of drying, transportation, volume availability,
513 synthetic pathway in accordance with green chemistry principles, life of the object, potential
514 recycle, end-of-life treatment, to name but a few. The use of LCB residue as solid filler for
515 composite material production is another way to valorise biomass for material production with
516 potentially a lower environmental impact than polymer production. Indeed, less transformation
517 (extraction, purification, polymerisation) should be required compared to the synthesis of
518 polymers from BSG-derived monomers. However, the percentage of fillers that can be
519 incorporated might be limited, as the materials could suffer from property losses, higher water
520 intake, strong colouration, etc.

521 **6.1 Polymers**

522 As hemicellulose is the easiest fraction to recover from the BSG matrix, its use as starting
523 material for polymer synthesis is an appealing strategy. However, polymeric or oligomeric
524 hemicellulose exhibit weak properties requiring plasticisation, blending with another material or
525 chemical modification [60]. One example was proposed by Farhat et al. with an extraction of
526 polymeric hemicellulose under alkaline conditions, followed by its crosslinking in presence of
527 zirconium to obtain hydro-resistant gels [72]. Similarly, Lu et al. described the functionalisation
528 of polymeric hemicellulose through etherification, esterification or branching using acrylamides
529 (graft copolymerisation). A strategy was presented to improve hydrophobicity of such polymers
530 by crosslinking hemicellulose using polyacids such as citric, oxalic, maleic or succinic acids [60].

531 Moreirinha et al. used two fractions of the LCB through arabinoxylan suspensions from BSG, mixed
532 with NFC (Nano-Fibrillated Cellulose), yielding films with antioxidant, antibacterial and antifungal
533 properties [112]. Similarly, a combination of cellulose and polymeric arabinoxylans from BSG can
534 also be used for food packaging production with good mechanical and thermal stability [27].

535 Qazanfarzadeh et al. recently reviewed the fractionation of BSG's matrix comparing various
536 biorefinery strategies with the use of each fraction for films and coatings applications in the food
537 packaging sector, showing the potential of this promising renewable resource [27]. The mixture
538 of lignin, hemicellulose and cellulose proved to be difficult to use as such for film forming
539 application, requiring separation, ideally with high purity to improve the properties of the
540 respective biopolymers. Thanks to its high intrinsic mechanical and water-resistant properties,
541 cellulose can be used by itself for film and coating applications or mixed with other compounds
542 like naringin to improve UV-blocking and barrier properties for example [113]. Using the
543 cellulosic fraction after its isolation in alkaline conditions followed by bleaching, dos Santos et al.
544 reported its conversion in a microwave reactor to the functionalised polymer CMC (Carboxy
545 Methyl Cellulose) (Figure 6) [114]. The two-step formation of the CMC was optimised using a
546 design of experiment, offering a greener pathway compared to the industrial method with a broad
547 spectrum of applications: paper, textile, pharmaceutical, paint and food sector.



548

549 **Figure 6** Visual transformation of BSG fibres (a), alkali-treated BSG (b), bleached BSG (c) and
550 carboxymethyl cellulose from BSG (d) under scanning electron micrograph (x1500) from dos
551 Santos et al. [114]. Reprinted from D. M. dos Santos, A. de L. Bukzem, D. P. R. Ascheri, R. Signini, G. L. B. de
552 Aquino, *Microwave-assisted carboxymethylation of cellulose extracted from brewer's spent grain*, 2015, with
553 permission from Elsevier.

554 Apart from carbohydrate fractions of BSG, Lee et al. used proteins from BSG (3 %) alongside
555 chitosan (2 %), mixed with glycerol to form films with antioxidant and antimicrobial properties
556 [115]. The protein fraction can also be used for film-forming applications under their polymeric
557 form, showing promising mechanical and antioxidant properties when formulated with PEG [27].

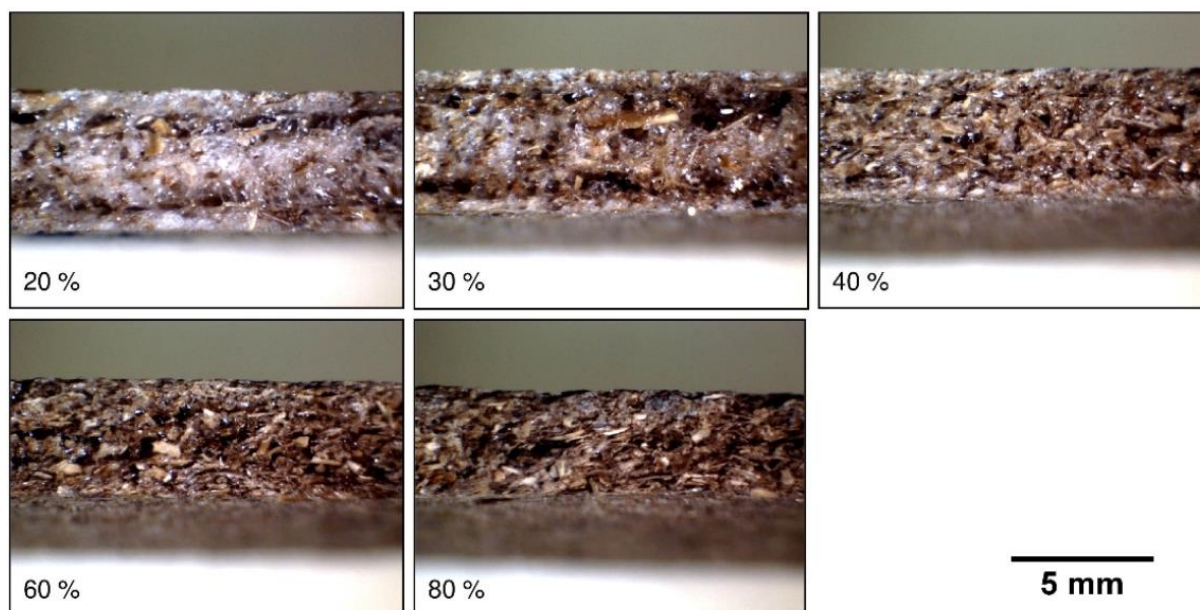
558 Despite the growing interest around the chemical valorisation of BSG, only a few examples
559 of biopolymer synthesis are described so far. The examples described herein show the potential
560 of this biomass for various application: gels, films and coatings, NFC, CMC. However, BSG's
561 flourishing valorisation could be extended by using the myriad of studies reported on other
562 lignocellulosic biomasses for the production of biobased polymers and composites. Examples of
563 polymeric materials produced from various lignocellulosic sources include cellulose acetate,
564 microfibrillated (MFC) or nanofibrillated cellulose (NFC), cellulose nanocrystals (CNC), drug
565 delivery polymers, packaging films from hemicellulose or lignin (antioxidant active packaging),
566 hydrogels, lignin-based carbon nanotubes [116, 117]. Polymers from lignocellulosic biomass can
567 also be blended together or blended with other bio-based or petroleum-based polymer matrixes
568 for further adaptability and scope of applications [118].

569 **6.2 Composite materials**

570 According to the literature, BSG can be used as a replacement of other biomasses such as
571 sawdust or wood particles for already know composite materials. Several studies have been
572 reported with BSG introduced as filler for construction materials, such as bricks (3.5-15 wt% of
573 BSG) [43], or for the production of particle board with unaltered properties if the amount of BSG
574 was kept below 10 wt% [119]. It was also used as a sawdust replacement for isocyanate composite
575 materials but resulted in a performance decline with properties being halved due to BSG's
576 presence [120]. Polyurethane and polyisocyanate foams have also been mixed with 16.7 wt% BSG
577 for applications in thermal insulation but the authors focused more on the polymer matrix
578 properties rather than the impact of the filler [121].

579 Ferreira et al. designed composite materials from BSG and potato starch by hot pressing to
580 produce inexpensive natural composite materials, to be compared with EPS (extended
581 polystyrene). Several BSG percentage were investigated yielding materials with higher flexural
582 strength and rigidity than the standard EPS (Figure 7). However, it was shown that these materials
583 were prone to water uptake, drastically reducing their performances. The addition of a
584 crosslinker, chitosan or glyoxal, or the coating of the produced trays with beeswax were proposed

585 as innovative strategies and successfully reduced water absorption (59.6 % reduction for
586 beeswax) and avoided the drop in performances previously observed [122]. Similarly, Hejna et al.
587 developed BSG/Mater-Bi polymer composites (biopolymers from starch and protein), to improve
588 the resistance of thermoplastic starch. Even when strengthening the composites by chemical
589 treatment with di-isocyanates, the composites revealed to be very sensitive to water, with weak
590 mechanical properties and thermal stability despite an improved biodegradability profile [123,
591 124]. BSG's fibres (1-5 wt%) were also introduced in starch film by Castanho et al. to improve
592 tensile strength and thermal stability [125].



593
594 **Figure 7** Pictures of biosourced composite trays from potato starch and BSG using 20 to 80 % of the BSG
595 filler prepared by Ferreira et al. [122]. Reprinted from A. M. Ferreira, J. Martins, L. H. Carvalho, F. D.
596 Magalhães, *Biosourced Disposable Trays Made of Brewer's Spent Grain and Potato Starch, Microwave-assisted*
597 *carboxymethylation of cellulose extracted from brewer's spent grain, 2019, with permission from MDPI.*

598 BSG can also be used as filler for composite materials using more traditional plastics. Revert
599 et al. prepared composite materials by extrusion of a PP matrix containing 10-40 wt% of BSG. The
600 introduction of BSG required a lower operating temperature to avoid combustion risk, as the
601 degradation observed with TGA was found between 250-350°C. The obtained material showed
602 lower mechanical resistance compared to neat PP but a higher thermal stability. Even though
603 water absorption is a common issue when using lignocellulosic fillers such as BSG, its introduction
604 in the PP matrix revealed a low absorption (< 6 %) [126]. Further examples can be found with
605 new composite materials being developed by industry, such as the biodegradable composite
606 materials proposed with a PLA matrix containing 5-30 wt% BSG. However, these materials exhibit
607 a low thermal resistance with a temperature of use below 50°C [127]. Additionally, BSG can be
608 used in combination with other fillers for hybrid filler composite materials. This strategy was used
609 by Formela et al. and Zelder et al. to develop materials using a mix of BSG and GTR (Ground Tire
610 Rubber) to replace natural rubber or to be introduced in a polyurethane matrix. However, the

611 introduction of BSG resulted in diminished properties, which could partially be counterbalanced
612 by the addition of GTR [128, 129].

613 Finally, Hejna et al. have studied in detail the impact of BSG as filler with various polymer
614 matrixes (NFC, PCL), and the interactions with them [130, 131]. They showed that the proteins
615 contained in BSG improved the interfacial compatibility by participating in Maillard reactions to
616 form melanoidins. Extrusion temperature was found to be the most determining factor for these
617 reactions, more present at higher temperature ($> 180^{\circ}\text{C}$), doubling the antioxidant power but
618 bringing a strong brown colouration of the polymers. However, despite the good compatibility,
619 BSG addition showed to be detrimental for mechanical and thermal performances. Furthermore,
620 terpenes and terpenoids were liberated during the extrusion step that can be harmful for human
621 health and the environment.

622 The use of BSG as filler could allow the valorisation of large amounts of this inexpensive and
623 sustainable by-product of the agrifood industry but in reality, the percentage that can be
624 introduced in polymer matrixes is limited to avoid impairing the thermomechanical performances
625 and water resistance. A few examples with successful results were nonetheless listed, requiring
626 improvements with coating or strengthening steps, to fully take advantage of the intrinsic
627 antioxidant and antimicrobial properties of this functional filler [126]. These challenges will need
628 to be addressed and compared to the results of other biomasses to understand better the potential
629 of BSG as natural filler in composite materials.

630 Similarly to polymer synthesis, BSG's valorisation could be improved by applying developed
631 strategies of valorisation from other lignocellulosic biomass, especially the ones close in terms of
632 composition, structure and properties like wheat straw. For example, hybrid wheat/clay
633 composites were fabricated to compensate the loss of properties and increased water sensibility
634 brought by the lignocellulosic biomass [132, 133]. More generally, the removal of amorphous
635 fraction of the lignocellulosic biomass could prove to be beneficial for the properties and water
636 absorption issues brought by such biomasses [134]. Some parts of the lignocellulosic biomass
637 could also be used for efficient material production. For example, lignin could be used as a cheaper
638 and more sustainable alternative to produce carbon fibres, replacing polyacrylonitrile (PAN)
639 based ones. Yadav et al. recently reviewed the potential of such lignin carbon fibre, and despite its
640 slightly lower performances compared to PAN, the lower cost and sustainability remain attractive
641 [135]. Similarly, Schneider et al. described the use of lignin for the production of lignin
642 nanoparticles for applications such as drug delivery, water treatment, nanofillers or antioxidant
643 materials [136]. Zhao et al. also described the production and use of such lignin nanoparticles
644 from similar biomass (wheat straw black liquor), a strategy that could be applied to Brewer's
645 spent grain [137]. All-cellulose composites (ACCs), where a regenerated cellulose acts as matrix,

646 reinforced with undissolved cellulose, is another great strategy to valorise one of the
647 lignocellulosic fractions for material production. The ACCs present a good compatibility between
648 the matrix and the filler and exhibit rapid biodegradation [138].

649 **7 Comparison with other lignocellulosic biomasses**

650 Comparison of valorisation efficiency or functionalised polymers performances can prove
651 to be challenging due to the difference in process conditions or overall properties of the materials.
652 Nevertheless, a few examples are described below to assess the potential of BSG compared to
653 other biomasses.

654 Concerning the production of hemicellulose, and thanks to the structural advantages of BSG
655 listed above, Mäki-Arvela et al. [44] showed that xylose yield from biomasses hemicelluloses was
656 most efficient when using BSG. Amongst wheat straw, rice straw, corn cob or stover, olive residue,
657 sugar cane bagasse, softwood chips, eucalyptus chips, southern red oak, oak hardwood, aspen
658 wood, poplar and BSG, the highest xylose yield was found for wheat straw (97 %, 720 min, 90 °C)
659 but the method used for BSG proved to be more efficient yielding xylose with 94.2 % in 37 minutes
660 at 140 °C. These 2 biomasses proved to be the most promising for xylose production compared to
661 other agrifood wastes and even more when compared to wood derived biomasses.

662 Similarly, lignin extraction from BSG or olive tree pruning using DES showed higher
663 efficiency for the former: 54.5 % extraction yield against 37.8 % for the latter. BSG's derived lignin
664 also showed a higher oxidant activity than its olive counterpart [93]. When comparing several
665 agrifood waste, namely BSG, spent coffee grounds (SCG) and kale, for the production of protein-
666 rich extracts with anti-oxidant capacity, Barrios et al. [139] showed that BSG exhibited the highest
667 yield and production flow, 14.6 kg/100 kg DM (94 % protein recovery yield) and 2.2 kg/h
668 respectively, compared to SCG (14.6 kg/100 kg DM, 2.2 kg/h) and kale (10.6 kg/100 kg DM and
669 1.6 kg/h), showing the competitiveness of BSG for such applications.

670 A comparison of PP/biomass composites is presented in Table 4, focusing on brewer's spent
671 grain, pine nutshell and corn straw in polypropylene matrix. For each property, the same
672 percentage of filler is used for relevant comparison, even though pine nutshell and corn straw
673 composites are prepared with 5 wt% compatibilizer [140], against 2 wt% for BSG [126], which
674 could explain the slightly higher water uptake for the latter. Overall, compared properties are in
675 similar ranges, showing the relevance of BSG to be used for such composites. Finally, compared to
676 wood chips biomass for the manufacturing of particleboard, BSG materials was found to exhibit a
677 higher initial water uptake after 2 hours, but a lower final water uptake and thickness swelling
678 after 24 hours [119].

679 **Table 4** Thermomechanical properties comparison between PP/biomass composites [126, 140].

	TGA starting degradation temperature (°C)	Tensile strength (MPa)	Water absorption (%)
Filler wt%	40	20	20
BSG	246	21	3.5
Pine nutshell	200	25.44	1.23
Corn straw	200	22.6	1.89

680 **8 Techno-economic feasibility and sustainability of BSG's valorisation**

681 **8.1 BSG's regulation**

682 Biopolymers obtained from BSG such as food packaging are biodegradable, but the EU has
683 not fixed the biodegradability limits for such bio-based materials. Furthermore, their degradation
684 might still be prone to nanoparticle formation and have an acidification and eutrophication impact
685 on the environment [27]. These matters will need to be addressed for an in-depth understanding
686 of the safety and potential of such biopolymers and composites.

687 **8.2 Safety standards**

688 While BSG's handling and transportation does not present any safety issue, its high moisture
689 content (70-80 wt%) makes it highly sensible to mould and bacteria development, with a shelf life
690 of 2-10 days depending on storage conditions [22]. To facilitate its use, this biomass is often dried,
691 significantly increasing its market price and environmental impact. However, during the
692 processing of BSG as filler in polymer matrix, using twin-screw extrusion for example, the
693 liberation of toxic terpene and terpenoid VOCs was observed and might represent a human or
694 environmental threat. These compounds were not yet quantified but the tuning of processing
695 parameters such as temperature appears to be important to reduce their liberation [131].

696 **8.3 Economic feasibility (cost benefit, market demand, competitiveness)**

697 In terms of land usage, BSG does not compete with crops for food growing, as it is regarded
698 as a waste or by-product from the agrifood industry. Even though the main use for BSG (70 %) is
699 represented by animal feed, allowing to valorise large quantities of this by-product, the chemical
700 valorisation of BSG for high value applications such as biopolymers or composite materials would
701 not compete with this sector. Indeed, the entirety of BSG's biomass is still not fully utilised to this
702 date, with 20 % ending in landfills with a loss of economically valuable resources and a non-
703 negligible environmental impact [22].

704 In terms of cost of the raw material, when comparing several crops feedstocks (BSG, corn
705 cobs, oat, rice, wheat and rye straws, soya and sunflower stalks), BSG (with hypothesis that it is
706 sold as-is with its initial moisture content) was found to have the lowest market price, 40 USD/ton

707 against 50-150 USD/ton for other agrifood wastes (2014) [20]. However, these values can vary
708 significantly depending on local agricultural and industry model as well as supply chain.
709 Furthermore, the authors underline the challenge of its high moisture content, meaning that the
710 valorisation strategies of BSG using the wet biomass would be preferable for optimised efficiency
711 and economic viability [20].

712 Concerning the promising building blocks obtainable from BSG, Mussatto et al. described a
713 biorefinery economic modelisation within the Brazilian economic system. From the models
714 investigated, full mass of water and energy integration appeared to be the best economic and
715 environmental impact model, yielding a 62.3 % economic margin (Figure 4) [21]. This resulted in
716 competitive prices of xylitol: 0.81-1.36 USD/kg, lactic acid: 0.86-1.26 USD/kg and phenolic acid:
717 22.14-32.72 USD/kg [21]. Further improvements were brought by Dávila et al. with a production
718 strategy yielding xylitol with a production cost of 0.35 USD/kg, lower than its market value (2.95
719 USD/kg). This shows the viability and potential of BSG for building blocks production, to be used
720 for biopolymer synthesis for example. However, the production of poly(hydroxybutyrate) (PHB)
721 was obtained with a cost of 3.36 USD/kg, higher than its market value [105]. As a comparison, the
722 production of lactic acid from other lignocellulosic biomasses such as corn stover or miscanthus
723 resulted in a price range of 0.99-1.39 USD/kg [141], slightly higher than BSG. Concerning xylitol,
724 produced from BSG with production costs of 0.35 USD/kg under the beet conditions [105], proved
725 to be very competitive compared to other biomasses ranging from 0.46 USD/kg (oil palm rachis)
726 to 22 USD/kg (spent blackberry pulp), amongst banana peel, corn stover, sugarcane bagasse, olive
727 tree crops and olive stones. Zeko-Pivač et al investigated the market size and growth rate (CAGR)
728 of the main building blocks that can be obtained from BSG, showing that most of these compounds
729 are expected to be prone to significant market share growth, such as lactic acid with an increase
730 of its market share increasing 3-fold from 2020 to 2030, and about a 1.5 fold for xylitol [13].
731 According to Barrios et al., when comparing the production cost of protein-enriched extracts from
732 BSG, SCG and kale, BSG showed the lowest production cost: 29.9 €/kg against 104.6 €/kg from
733 SCG and 45.5 €/kg for kale. Despite minimum selling prices exceeding the estimated sale price of
734 such products, BSG proved to be the most competitive compared to other biomasses. (Barrios-
735 2022) [139].

736 BSG proved to be economically viable for most of the applications and highly competitive
737 compared to other biomasses: agrifood wastes or wood derivatives. However, the use of BSG in
738 biorefineries is still scarce and the development of improved or new valorisation routes would
739 allow to improve the economic feasibility of BSG valorisation within biorefineries [28, 142]. More
740 specifically, little information is available on the economic potential of BSG's application for
741 polymers or composites. As the production of building blocks appears to be competitive with the

742 market prices, it is reasonable to assume that polymers issued from these building blocks would
743 be economically relevant subsequently. The new valorisation strategies developed in the future
744 will need to be investigated in this regard.

745 **8.4 Sustainability (environmental impact, LCA)**

746 As exposed, BSG's valorisation is not fully sustainable to this date due to the impact of
747 landfilling of 20 % of this agrifood waste. This last option to dispose of the BSG equates to an
748 environmental impact of $\text{CO}_2_{\text{eqv}} = 513 \text{ kg/t}_{\text{BSG}}$ [29]. The economic and environmental impact of this
749 drying step needs to be minimised for optimal valorisation of BSG [25] and the use of wet BSG
750 [46] would be preferable. However, avoiding the drying of the high moisture content biomass to
751 significantly reduce the environmental footprint linked to its valorisation would require
752 logistical adjustments for BSG transportation to prevent the logistic impact to counterbalance the
753 usage of wet BSG [143].

754 Similarly to the economic viability aspect, the chemical valorisation routes have yet rarely
755 been the subject of in-depth sustainability investigation such as LCA, especially concerning
756 polymers and composites. From the biorefinery models for the production of xylitol, lactic acid,
757 activated carbon and phenolic acids developed by Mussatto et al. (Figure 4), the most
758 economically viable option also resulted in the lowest environmental impact with a PEI = 0.012
759 /kg of products and a processing carbon footprint of 0.96 kg $\text{CO}_2\text{eq/kg}$ of BSG [21]. Similarly to
760 the economic point of view, the optimised strategy proposed by Dávila et al. allowed to reduce the
761 global warming potential with an impact for the production of xylitol of $5.5 \cdot 10^{-5}$ PEI/kg and
762 $6.93 \cdot 10^{-4}$ PEI/kg for PHB [105]. An in-depth cradle to grave sustainability assessment has recently
763 been presented by Tiwari et al. on the microbial production of 2,3-butanediol (BDO) from BSG
764 giving a carbon footprint of 7.25 kg CO_2/kg BDO with the cultivation stage having the largest
765 impact, alongside transportation. It also showed that the production of such building block
766 (butanediols) from biomass (BSG or wheat straw) exhibited a lower impact compared to the
767 fossil-based production of butanediol [144]. Concerning BDO production, values reported for
768 other biomasses are 2.82 kg CO_2/kg BDO for cardoon and 5 kg CO_2/kg BDO for wheat straw but
769 correspond to the production of the 1,4-BDO isomer [144].

770 For building blocks, polymer and composite application, work remains to be carried to fully
771 assess the potential of this biomass from the sustainability point of view. In terms of
772 biodegradability, BSG's sourced polymers and composite materials mainly show good
773 biodegradation profiles [124].

774 **8.5 Scaling-up: from the lab to the industry**

775 Apart from valorisation routes for animal feed or biofuel production that have been
776 optimised throughout the years, BSG's valorisation for biopolymers or composites are still far
777 from being efficiently introduced in biorefineries for an optimal valorisation [145]. Biorefinery
778 models such as the one described by Mussatto et al. [21] are good indicators on the potential
779 economic feasibility of such valorisation routes on larger scales with a BSG feedstock scale of 100
780 t/h. An efficient fractionation of BSG's LCB on a large scale (1 ton) was also described by De Crane
781 d'Heyselaer et al. [102].

782 **9 Challenges and future directions**

783 Several challenges and obstacles were outlined within this review that will need to be solved
784 in the future for an optimal valorisation of this promising bioresource. Firstly, the use of dried BSG
785 results in a significant carbon footprint (drying) and the use of the wet biomass would be
786 preferable, while keeping in mind the perishability, the need for particle size reduction and the
787 logistic adjustment that it implies. New strategies, especially regarding the obtention of valuable
788 building blocks and their transformation into biopolymers are required to diversify the options in
789 terms of building blocks and platform molecules availability, as well as final polymer properties.
790 The scale up of such chemical upcycling route has seen little interest this far but is paramount for
791 the integration of such valorisation strategies within biorefineries to facilitate higher value
792 valorisation. The economic and environmental impact have started to be investigated, but more
793 comprehensive studies are still required to evaluate the economic impact of such valorisations for
794 breweries, their economic feasibility in a context of biorefinery, the environmental impact
795 through LCA for example, as well as the comparison of above-mentioned criteria with different
796 biomass valorisations. So far, LCA have mostly been conducted for food application and very
797 recently started to be shared for a few building blocks [144] but not yet on BSG's valorisation for
798 polymer applications or composite materials. New strategies of valorisation for building block
799 production, polymer or composite material that will be developed in the future will need to
800 evaluate the scalability of proposed valorisation routes, their economic viability, environmental
801 impact while comparing their performances in regard to previously designed materials using
802 other lignocellulosic biomasses for example.

803 For an application as natural filler, the introduction of BSG often proved to be detrimental
804 for the final material and the development of new strategies are required. The removal of the
805 lower-properties fractions like hemicellulose from the lignocellulosic biomass, could help in this
806 regard, to improve the properties of this functional filler and reduce the decrease in properties
807 and increased water sensibility observed in most examples of such biomass valorisation. In
808 conclusion, to valorise large amounts of BSG, a combination of both polymer and composite

809 material approaches could be ideal. A part of BSG's lignocellulosic biomass could be fractionated
810 and valorised as polymeric matrix of high-performance, non-toxic or ecotoxic, biodegradable
811 polymers, to which the rest of the biomass could be added as renewable filler. This strategy could
812 help upcycle this waste biomass in larger amounts while using BSG as a whole in a biorefinery
813 strategy without compromising the final properties (physicochemical and water resistance). Such
814 biorefineries have to be modelised to help provide high value products while targeting carbon
815 neutrality throughout the valorisation process.

816 **10 Conclusion**

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

827 Conditions reported in the literature for the extraction and degradation of each fraction
828 (hemicellulose, cellulose, lignin, protein) of BSG's lignocellulosic matrix were reviewed alongside
829 full fractionation examples for BSG or similar biomasses. This shows that many different
830 conditions can be used depending on the biorefinery strategy and the desired form of each fraction
831 (polymeric, oligomeric, monomeric). However, the conditions used for each step might have a
832 significant impact on the subsequent conditions as it could alter the structural organisation of
833 the remaining fractions. Available building blocks obtained from the extraction and degradation
834 of BSG's fractions were described. Furthermore, their use as starting materials for useful
835 monomer or polymer synthesis was discussed. Only a few examples of BSG's chemical valorisation
836 for polymer applications have been presented so far, but the examples listed herein show great
837 potential. BSG's use as natural filler was also reviewed but its introduction often resulted in
838 inferior properties and performance as well as increased water sensibility. Post treatments helped
839 to mitigate these properties drops but BSG's percentage was often limited to 10-20 wt% or even
840 less.

841 Finally, the challenges and potential directions of investigation were discussed, reviewing
842 the necessary steps towards a more efficient valorisation of this promising brewing by-product.

843 More precisely, comprehensive studies on the environmental impact, economic feasibility and
844 scalability of developed valorisation routes or future strategies are of prime importance. A lot has
845 yet to be achieved to this end, but the environmental, economic and societal output are driving
846 forces considering the global amount produced as well as the current valorisation options
847 available.

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1207
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