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

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

Barley and BSG

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

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

BSG is an inexpensive raw material with an estimated cost around 35€/t of dry matter [13] or 42 USD/t [16]. Its all-year-round availability and low cost make it an interesting resource for various applications. However, it is rapidly perishable due to microbiological instability: high MC and presence of fermentable sugars, with a shelf life of 2-10 days depending on storage conditions. [17] Due to its high moisture content, the major part of its cost is brought by the transport [18] but mainly by the drying process of this biomass [16] with a high environmental impact of 495-770 kg_{CO2}/t_{BSG} (CO_2 equivalents) for the latter. Arranz et al. have developed a solar oven as an alternative to conventional drying techniques for BSG (convection drying [19] or infra-red drying [20]), lowering the environmental impact to 0 kg_{CO2}/t_{BSG} but increasing the drying time 10-fold. [18] The elimination of the water contained in renewable biomass is a major challenge that needs to be taken into account when designing valorisation routes to prevent having a greater environmental impact than the petroleum-based counterpart they try to supplement. Examples of biomass valorisation have shown that water elimination can cover up to 80% of the energy cost, before the actual valorisation process even begins. [21] Thus, an LCA (Life Cycle Analysis) should be performed when possible to confirm the benefit of such routes and new materials. By assessing the techno-economic feasibility, the environmental impacts and energy consumption of BSG's valorisation, a recent study showed that water removal was indeed an important step of the process in terms of environmental impact, advocating mechanical dewatering such as screw, centrifugal, hydraulic or membrane filter presses. Without eliminating the risk of microbial growth of BSG like a complete drying would, the mechanical dewatering should prolongate the shelf-life of BSG before its valorisation, that can be as low as 48 hours for wet BSG (with around 80% WC). Alternative drying methods such as microwave drying could eliminate water with a limited CO_2 emission, reaching moisture levels below 10%. [22]

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

dispose of the BSG waste equates to an **environmental impact of $CO_{2\ eqv}$ =513 kg/t_{BSG}**. [24] It would thus be important to valorise this resource more efficiently by producing higher value products that would encourage breweries to further upcycle this resource.

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

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

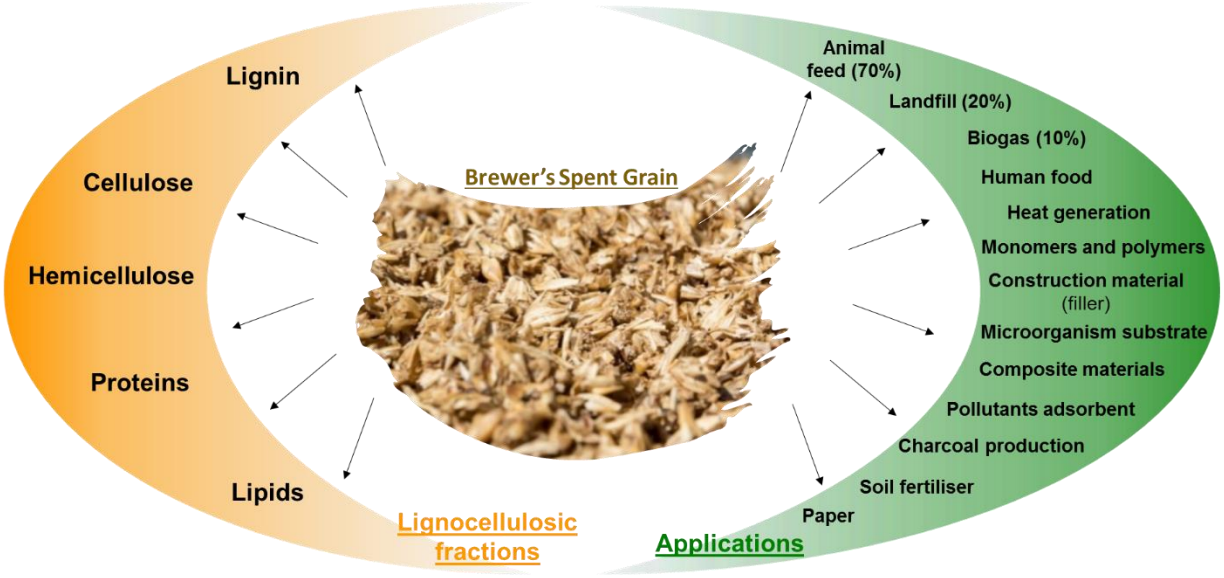

Figure 1 Fractions present in BSG's lignocellulosic biomass and their potential applications.

2 Composition

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

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

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

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

3 Applications

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

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

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

- **Heat generation:** The most efficient way to use BSG for combustion application is under pellet form and could be used directly as fuel for heat production in microbreweries. [51] Its calorific value equals **9.6-11.3 MJ/kg** [54], similar compared to other bio-fuels for combustion. [19] However, this requires a costly preliminary drying step and its combustion liberates particles and toxic gases: NOx and SOx, 480 and 1000-3000 mg/m^3 respectively. [19] [39] Recently, a hydrochar from BSG was prepared through microwave-assisted hydrothermal carbonisation, reported with a high calorific value: 32 MJ/kg [52], alongside a bio-oil fraction (26 MJ/kg) and a saccharide-rich aqueous fraction. [53]
- **Other applications:** The valorisation of BSG for the production of biodiesel, biogas, bioethanol, biohydrogen or biobutanol has recently attracted the interest of the scientific community. [51] Otherwise, its carbonisation followed by an activation allows the production of activated charcoal. Other reported usage of BSG mention paper production, as adsorbent for pollutant and dyes elimination in water, substrate for microorganism and yeast, fungi growth or as soil fertilisers. [39] [54]

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

4 Biomass fractionation

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

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

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

4.1 Hemicellulose extraction

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

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

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

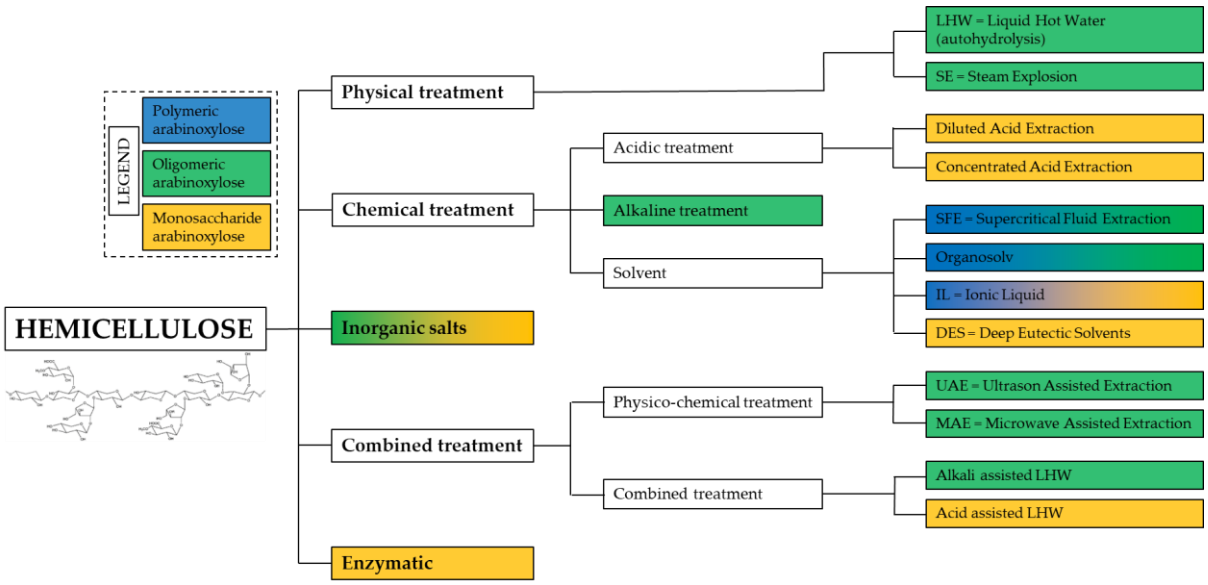

Figure 2 Different hemicellulose extraction processes with the form of the final product (polymeric, oligomeric or monosaccharide).

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

Treatment	References	Arabinoxylose form	Selectivity and efficacity
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.

Alkaline treatment	[56] [65]	Oligomeric: 49200-64300 g/mol	Saponification at 80-150 °C between ferulic acid from lignin and AX, liberating hemicellulose in high yields.
SFE	[4] [56] [66]	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	[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.
IL	[67] [58]	Polymeric/ monosaccharide	[Amin]Cl used to break H-bonding and liberate AX (75 % yield) under polymeric form except for [C_2mim][OAc] liberating monosaccharides. Difficult to separate products and IL to regenerate them.
DES	[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.
UAE	[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).
MAE	[56] [71]	Oligomeric	More efficient extraction than UAE: 1-5 min vs 10-30 min for UAE (77 % yield).
Inorganic salts	[58]	Oligomeric	Alternatives to acidic hydrolysis with less corrosion and recyclability issues using NaCl, KCl, $CaCl_2$, $MgCl_2$, $FeCl_2$, $ZnCl_2$, $FeSO_4$, **$FeCl_3$** (89 % yield).
Enzymatic	[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]

4.2 Saccharification of BSG (hemicellulose acidic treatment)

Diluted and **concentrated acidic extraction** (**DAE** and **CAE** respectively) allow the breakdown of hemicellulose into monosaccharide. Even though **stronger acidic conditions** improve the homogeneity of the reaction and allow the use of lower temperature and pressure, [40] it faces corrosion, acidic waste management and stronger degradation issues converting sugars into furanic moieties or humines. [61] Even though this decomposition can be slowed by adding protectors such as ethyl-ethyl ketone [40], these conditions are typically used for the more robust crystalline carbohydrate polymer, cellulose, to produce glucose using 10-30 % H_2SO_4 for example. These conditions can even be used to directly produce furanic derivates and optimised using MAE or UAE. [40]

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

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

Acid	Specificity and advantages
H_2SO_4	**Best reactivity and selectivity**
HCl	Reactivity similar to sulfuric acid but lower selectivity (glucan dissolution): preferred for cellulose degradation
HNO_3	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_3OH (carbon-based solid acid): allows the use of reduced temperature, water usage and corrosion issues
Phosphoric	-
Formic	-

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

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

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

4.3 Protein extraction

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

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

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

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

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

4.4 Lignin extraction

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

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

hemicellulose) in strong acidic conditions (10 M of H_2SO_4, HCl or acetic acid) and 5M NaOH and filtration, with the highest purity (98 % purity) and yields (82.9 % of the lignin contained in BSG, representing 5.6 wt% of the original composition) obtained when using H_2SO_4. [89] Characterisation of the extracted lignin showed good thermal stability with a T_g of 107 °C (H_2SO_4). Finally, organosolv treatment is a possible procedure to recover the degraded lignin within a black liquor. This was described by Parchami et al. after an acidic pre-treatment to eliminate the glucan-rich fraction. [90] The organosolv process conditions were optimised using 50 % v/v ethanol to obtain precipitated lignin with a 58 % yield and a 95 % purity.

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

4.5 Cellulose extraction

Few examples of cellulose extraction and valorisation from BSG are found in the literature due the more complex accessibility, especially opposed to BSG's hemicellulose, being the most easily extractable compared to other biomasses, and simple to convert to monomers of rare sugars. Matebie et al. used a conventional approach for the obtention of cellulose with 3 pre-treatments to remove hemicellulose and lignin: diluted acid hydrolysis, alkaline treatment, and bleaching. [92] The obtained cellulose was then converted into CNC (Cellulose NanoCrystals) using concentrated acid hydrolysis (51 wt% H_2SO_4). The synthesis parameters were optimised to yield cellulose with 43.24 % and a high crystallinity.

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

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

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

4.6 Biomass full fractionation

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

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

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

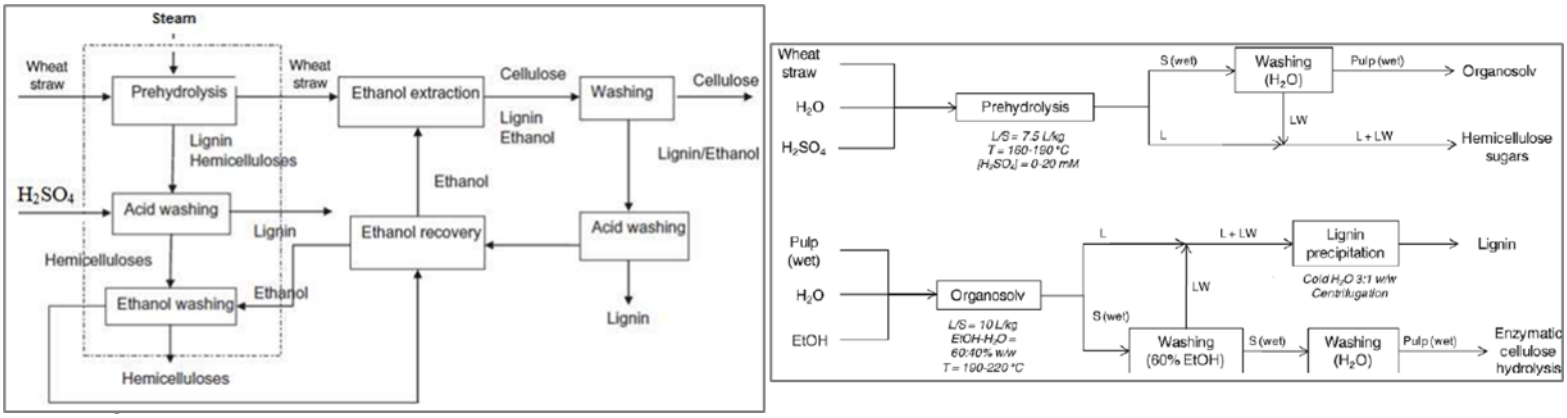

Figure 3 Lignocellulosic biomass fractionation flow chart (wheat straw) described by Ortega et al. (left) [67] et Liu et al. (right) [95] to separate hemicellulose, lignin and cellulose.

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

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

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

5 Building blocks from BSG

Few examples of chemical valorisation of BSG are reported in the literature with a full fractionation of BSG to obtain various building blocks of interest, as developed by Mussatto et al. and described below. [16] [99] As displayed in Figure 4, a DAE was used as an efficient mild pre-treatment using citric acid to extract 91.8 % of hemicellulose under monosaccharide form, yielding a xylose-rich hydrolysate. This fraction was in turn converted to xylitol with a 97.8 % yield, while the rest of the LCB was treated in alkaline solution for delignification, yielding phenolic acids and activated carbon after phosphoric acid activation and carbonisation. [16] The cellulose-containing solid fraction was fermented using *Lactobacillus delbrueckii* to transform 99 wt% of the glucose into lactic acid (LA) after adjusting the pH for optimal yield. [99] The economic feasibility of this strategy was validated by the biorefinery modelisation giving an economical margin of 62.25 % with a PEI (Potential Environmental Impact) of the process of 0.012 PEI/kg and a carbon footprint of 0.96 kg CO_2-e/kg of BSG. [16] This shows the potential of BSG as LCB to be chemically valorised, especially for polymer chemistry where these building blocks could be of high interest.

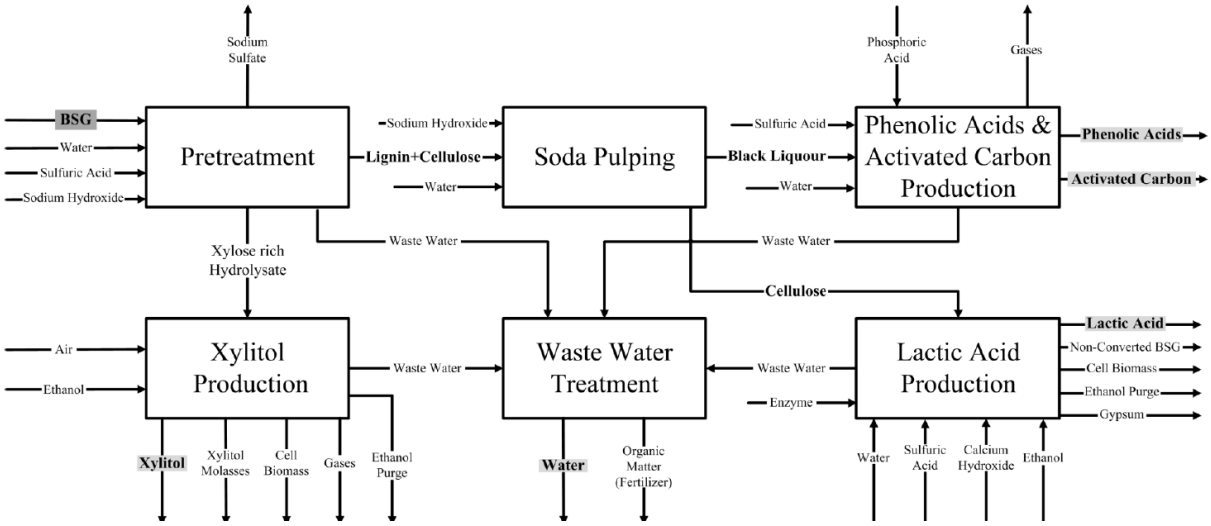

Figure 4 Full fractionation flowchart of BSG yielding various building blocks proposed by Mussatto et al. [16]

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

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

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

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

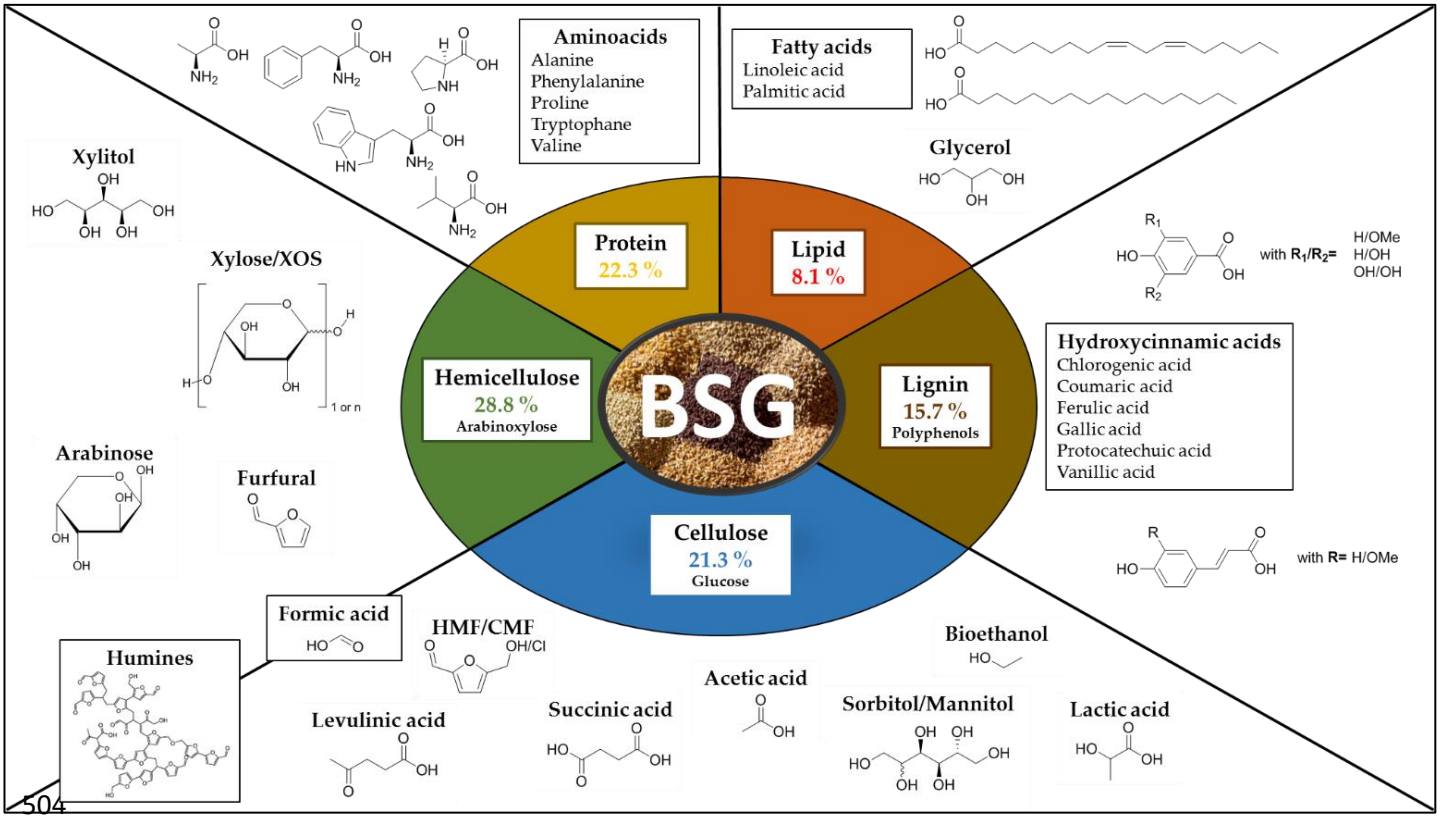

Figure 5 Overview of available building blocks obtainable from the BSG's LCB (percentage of each fraction given as mean values: Table 1).

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

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

6 Polymers and composite materials from BSG

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

6.1 Polymers

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

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

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

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

6.2 Composite materials

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

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

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

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

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

8 Conclusion

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

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

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

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

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679

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