



More than just a beer—the potential applications of by-products from beer manufacturing in polymer technology

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Abstract

Beer is the most popular alcoholic beverage in the world, and its popularity is continuously growing. Currently, global beer production is estimated at around 2 billion hectoliters. Nevertheless, the increasing production capacity implicates the rising issue of generated by-products—brewers' spent grain, spent hops, spent yeast, and wastewater. They are generated in massive amounts, so having in mind the current pro-ecological trends, it is crucial to look for their utilization methods. Among the possibilities, particular attention should be drawn to polymer technology. This sector can efficiently use different lignocellulosic materials, which could be applied as fillers for polymer composites or sources of particular chemical compounds. Moreover, due to their chemical composition, brewing industry by-products may be used as functional fillers and additives. They could be introduced to enhance the materials' resistance to oxidation, microbes, or fungi. These issues should be considered especially important in the case of biodegradable polymers, whose popularity is growing over the last years. This paper summarizes the literature reports related to the composition and potential applications of the brewing industry by-products in polymer technology. Moreover, potential directions of research based on the possibilities offered by the brewing industry by-products are presented.

Keywords Brewing by-products · Beer · Brewers' spent grain · Spent hops · Spent yeast · Trub · Wood polymer composites · Polymer materials

1 Introduction

As a process aimed at beer production, brewing is known for thousands of years [1]. Depending on the times and mainly the development of humanity and science, the specifics of this process were changing [2]. Figure 1 presents the current general scheme of beer production. Generally, the brewing process consists of the following stages, starting from the malt: crushing of malt, mashing, lautering, filtration, boiling, and fermentation. At first, malt is crushed to break apart the kernel and facilitate the extraction of sugars during mashing [3].

Then, crushed malt is mixed with hot water in a mash tun creating the cereal mash. Naturally occurring enzymes present in the malt convert the starch extracted from the malt into simpler fermentable and non-fermentable sugars

in the saccharification process [4]. To enhance the yield of mashing, in the end, the mas is often heated up to 76–78 °C, which is called mashout, and sprinkled with additional water during sparging [5]. Such processes are implemented to reduce mash viscosity, free up more starch, and extract additional sugars [6]. As a result, a sugar-rich liquid called wort is obtained after separation from the solid residue of mashing called the brewers' spent grain (BSG) [7].

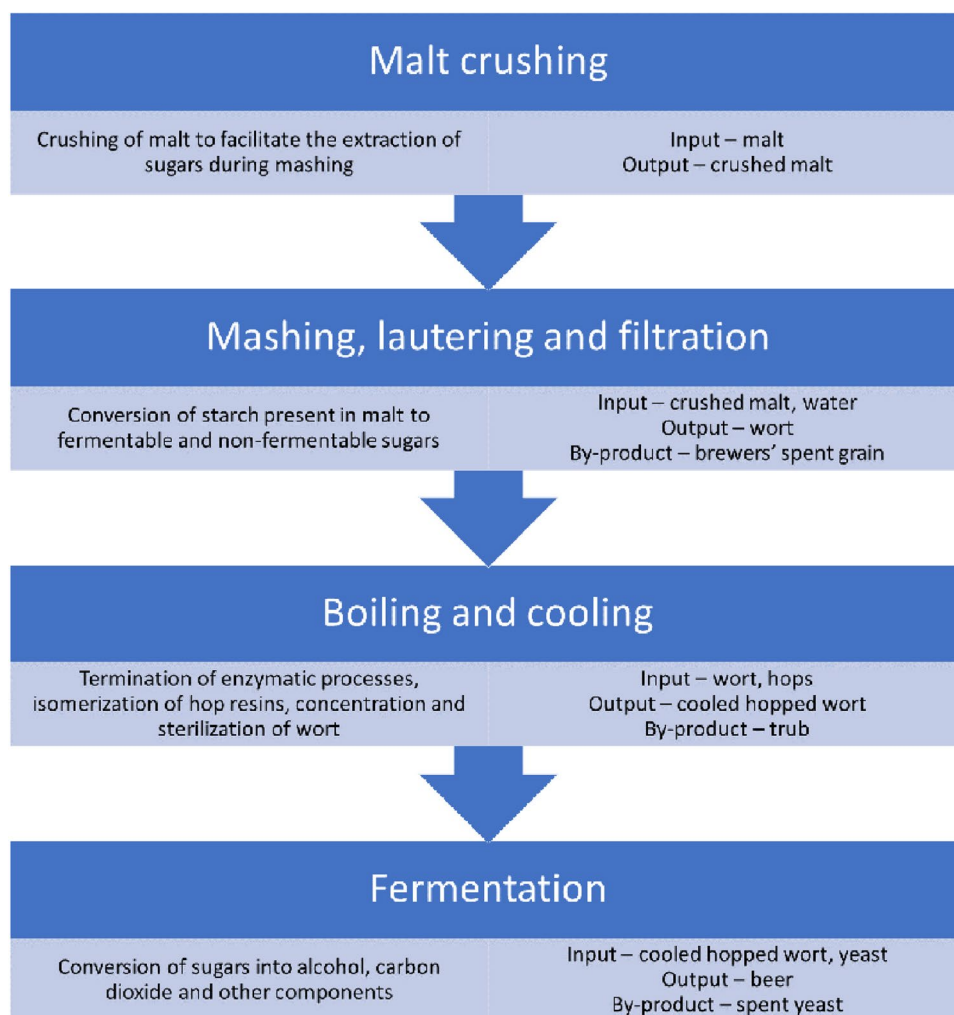
The wort is moved to the kettle, where it is boiled with hops (and sometimes other ingredients). The boiling process aims to terminate the enzymatic processes, precipitate proteins, concentrate and sterilize the wort, as well as extract compounds from hops to beer and isomerize hop resins to add bitterness to beer [8]. Moreover, boiling may induce caramelization and Maillard reactions in wort [9]. In the end, the hopped wort is cooled down and separated from the trub, which includes the hop residues and colloidal proteins coagulated during boiling [10].

Cooled and hopped wort is transferred to the fermentation tanks and pitched with yeast, converting the fermentable sugars into alcohol and carbon dioxide. Moreover,

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Fig. 1 The general scheme of beer production with an indication of generated by-products



depending on the type of yeast, different reactions occur, which account for the beer's final taste and aroma profile [11]. After complete fermentation, the beer is separated from the surplus yeast, called spent yeast, conditioned in the additional tank, and packed into bottles, casks, or cans [12].

2 Beer production statistics

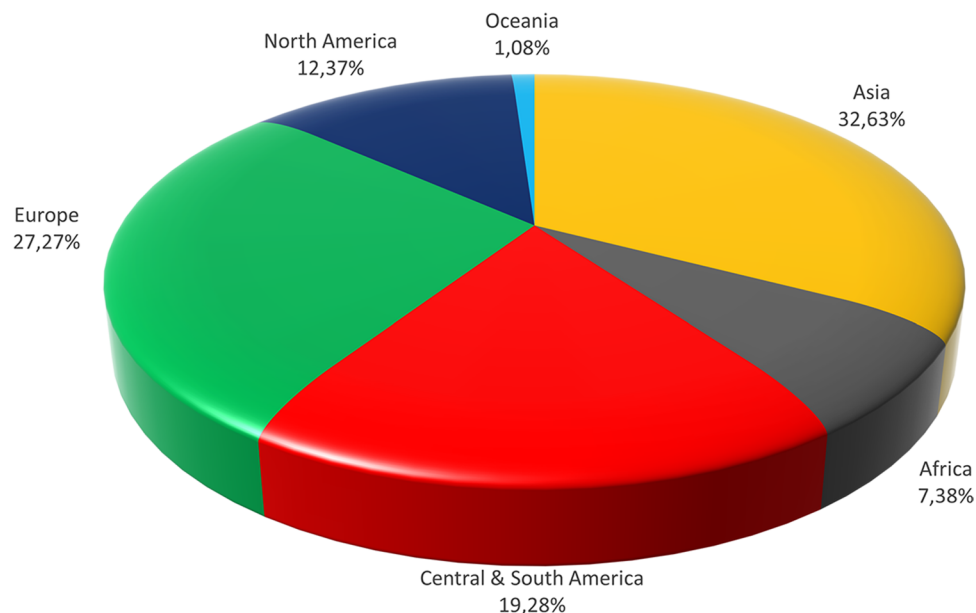
Beer is the most popular alcoholic beverage globally and the third most popular beverage after water and tea [13]. The global beer production size is relatively stable in the last decade and accounts for 1.91–1.97 billion hectoliters [13]. The leading producer is China, whose production in 2019 equaled 376.5 million hectoliters and accounted for ~20% of global production [14]. The Americas occupy the following positions—the United States, Brazil, and Mexico with 210.3, 144.8, and 124.2 million hectoliters, respectively [15]. Considering Europe, the size of production exceeds 420 million hectoliters annually [16]. The share of particular continents in the global beer production is presented in Fig. 2. The biggest

producer is Germany, the country with great brewing traditions. In 2019, Germans produced 91.6 million hectoliters of beer, mostly pilsener and wheat beer [17]. In Europe, Germany is followed by Poland and the UK, whose production is around 40 million hectoliters [18]. It is also essential to mention Russia as a critical producer with 77.4 million hectoliters produced in 2019 [19]. Russia is one of the few countries where beer is not the most popular alcoholic beverage, with a higher vodka share [20]. Presented data indicate that global beer production is distributed across all the regions of the world. Therefore, research activities related to the manufacturing, consumption, and health aspects and the utilization of by-products of beer production are essential because these aspects may affect an enormous number of people worldwide.

3 Beer production by-products

Conventionally, beer is produced from barley and, to a noticeably lesser extent, from wheat [21]. Such a production model is commonly applied in Europe. Moreover, in

Fig. 2 The share of particular continents in the global beer production



Germany, such issues are regulated by Germany's Beer Purity Law, originating from the medieval Bayreisches Reinheitsgebot [22]. Nevertheless, in different regions of the world, other starch sources are also applied, such as maize in America [23], rice in Asia [24], or sorghum in Africa [25]. Considering hops and yeast, their use is associated with the desired beer style. The market offers an enormous range of hops and yeast varieties [26, 27].

According to the brewing scheme presented in Fig. 1, the main by-products of beer manufacturing are the brewers' spent grain, trub removed after wort boiling, and spent yeast. The generation of brewing by-products is very similar globally, with possible differences in their composition, depending on the location. These materials are currently often unutilized and present hardly any market value. Generally, considering the current pro-environmental trends in scientific and industrial activities partially stimulated by the changing law regulations established worldwide, waste and by-products management are essential [28]. Except for the environmental motivations, the application of such materials in various production processes can generate added value for the resulting products (enhanced performance or new properties) or reduce their manufacturing costs [29].

One of the industry branches where by-products from beer manufacturing could be potentially applied in polymer technology. This sector of the industry is enormously dependent on petroleum price and availability [30]. It is commonly known that its resources are constantly shrinking, and it is essential to seek new raw materials, which could substitute petroleum, beneficially from renewable resources [31]. In the following sections, the literature reports on the applications of brewing by-products in polymer technology would be discussed.

3.1 Brewers' spent grain

3.1.1 Overview

The main and the most abundant by-product generated by the brewing industry is brewers' spent grain. It is generated in high amounts and accounts for over 85% of beer manufacturing by-products [32]. During the mashing process, around 69% of the initial malt mass is extracted and converted to sugars soluble in wort [33]. Considering that production of the one hectoliter of beer uses 20 kg of malt, around 6.2 kg of dry BSG is generated. Such values are typical for the most popular beer style worldwide—light lager [34]. Other beer styles, especially those characterized by higher original gravity, require higher malt loadings, even up to 45 kg for strong stouts or porters [35]. Keeping in mind the size of the global beer production, almost 12 million tonnes of brewers' spent grain is generated worldwide. The biggest producer, China, accounts for over 2.3 million tonnes, followed by the USA with 1.3 million tonnes, while European production generates around 2.6 million tonnes of BSG [34].

3.1.2 Composition

One of the main drawbacks of BSG as a potential raw material for other processes is its high moisture content, exceeding 75% [36]. Together with the presence of polysaccharides, this factor makes the BSG a perishable material. Drying of brewers' spent grain, which could be easily performed using conventional dryers, might noticeably enhance its attractiveness for other industry branches, including polymer technology [37]. Moreover, BSG is characterized by the relatively low activation energy values during drying, comparable to

other food industry by-products such as carrots, beans, or general vegetable waste [38]. The drying of BSG requires less energy than, e.g., olive processing by-products, probably due to their high lipid content [38].

The brewers' spent grain can be characterized by a similar composition to various lignocellulose materials except for the high moisture content. As presented in Table 1, the total content of carbohydrates in BSG is around 50%, which is noticeably lower compared to other lignocellulose waste materials, e.g., barley straw (56%) [39], rye, or oat straw (66–68%) [40], sunflower or cotton stalks (72–73%) [40]. Such a phenomenon is attributed to the partial reduction of carbohydrate content during mashing when starch is removed [41].

Moreover, brewers' spent grain contains from 10 to even 28% of lignin, depending on the reports [48] and a significant amount of proteins, which is attributed to their high content in barley grain [52]. The detailed composition of proteins in BSG may differ depending on the determination method, source of by-product, and applied malts, mostly crop species [33]. According to Robertson et al. [53], the glutamine is the primary amino acid of BSG (around 19–20% of total proteins), followed by a proline (~9%), asparagine, and leucine (both ~8%), arginine, phenylalanine, and valine (~7%). On the other hand, Waters et al. [54] reported that histidine is present in the highest amount exceeding 26% of total proteins, followed by glutamine (~16%), lysine (~14%), and leucine (~6%), while the content of other amino acids does not exceed 5%. Nevertheless, irrespectively of the detailed composition of amino acids, BSG should be considered as protein-rich material.

Brewers' spent grain often contains noticeable amounts of phenolics, which may provide additional value for various applications due to their antioxidant and antimicrobial properties [55]. The main phenolic components of BSG are hydroxycinnamic acids (HCAs) and hydroxybenzoic acids (HBAs), particularly ferulic, *p*-coumaric, sinapic, syringic, and caffeic acids [56–58]. The first two compounds are present in the highest amounts, but the literature reports indicate that their contents depend strongly on the type of malts used for brewing [59]. McCarthy et al. [59] showed

that the roasting of pale barley malt reduced the total HCAs content in BSG by 57%. Also, Moreira et al. [60] pointed to the reduction in total phenolic content due to increasing malt kilning temperature. For chocolate and black malts, kilned at temperatures exceeding 220 °C, the content of ferulic and *p*-coumaric acids was reduced by over 50%. The effect was significantly smaller for melanoidin and carared malts, which were subjected to a temperature in the range of 120–160 °C.

Generally, the structures of the major phenolic acids present in brewers' spent grain are presented in Fig. 3. Their detailed composition in particular BSG samples and other by-products, may noticeably differ depending on the method of their extraction, selection of solvents, and method of the quantitative analysis [35]. Nevertheless, despite the differences in reported contents of HCAs and other phenolics, they significantly enhance the antioxidant activity of BSG compared to other lignocellulose materials.

These compounds mentioned above present in BSG are considered strong antioxidants and may enhance the stability of polymeric materials [61–63]. Considering the antioxidant activity of BSG, it may contain noticeable amounts of melanoidins, mainly when it originated from the production of darker beers. Melanoidins are generated during Maillard

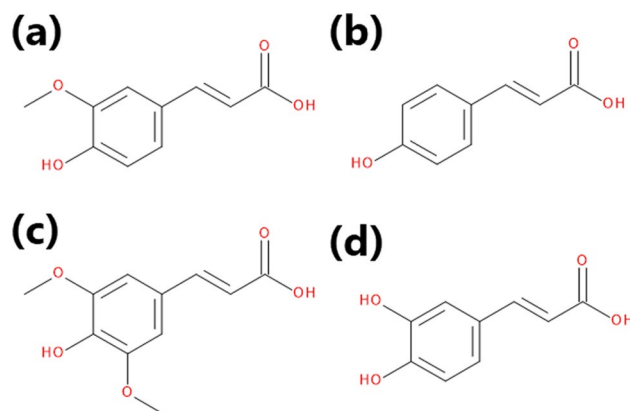


Fig. 3 The structures of the major phenolics of BSG: **a** ferulic, **b** *p*-coumaric, **c** sinapic, and **d** caffeic acid

Table 1 The composition of brewers' spent grain according to the literature reports

Component	Content, %dry matter										
Cellulose	–	–	–	25.4	23.0–25.0	16.8	22.2	12.0–25.0	21.9	12.0	21.7
Hemicellulose	–	–	–	–	30.0–35.0	28.4	26.8	20.0–25.0	29.6	40.0	19.2
Lignin	–	–	–	11.9	–	27.8	14.1	10.0–28.0	21.7	11.5	19.4
Ash	3.8	3.4	3.3	2.4	4.0–4.5	4.6	–	2.0–5.0	1.2	3.3	4.2
Proteins	26.9	21.8–26.4	26.7	24.0	19.0–23.0	15.3	–	19.0–30.0	24.6	14.2	24.7
Fat	–	3.6–5.8	–	10.6	–	–	–	10.0	–	13.0	–
Phenolics	–	1.6–2.0	–	–	–	–	–	–	–	2.0	–
Reference	42	43	44	45	46	47	41	48	49	50	51

reactions occurring between carbonyl groups of reducing sugars and amino groups of amino acids present in proteins [64]. As a result, the complex mixture of higher molecular weight oligomeric and polymeric compounds is obtained [65]. They are responsible for the browning reactions of various food products after applying temperature, e.g., during baking, frying, or cooking [66].

Moreover, the brewers' spent grain contains multiple micro- and macroelements, mostly silicon, phosphorous, calcium, and magnesium [32]. Combining their content with the presence of vitamins, primarily B3, B4, and B5, the BSG is often investigated in food additives [48, 67].

3.1.3 Current applications and potential in polymer technology

Animal feed Nowadays, the main application of brewers' spent grain is low-value animal feed with relatively low market value. It is often sold to farmers, mainly in a wet state [68]. It is associated with the composition of this by-product, particularly protein content [45]. As a result, Belibasakis and Tsirgogianni [69] and Sawadogo et al. [70] reported the enhanced milk production for cows fed with BSG. Also, other works reported the beneficial impact on animal nutrition, including fish, pigs, and chickens [71–73]. In the case of lack of potential recipients of BSG for animal feed, this by-product may be deposited in the fields, where in moderate amounts, it can act as natural fertilizer [55].

Human food Considering the nutrition, brewers' spent grain was also investigated as a human food ingredient. Because of its composition and origin, it was introduced into bakery products as a flour substitute [74]. Ground BSG is characterized by a darker color than the lightest types of flour, so it could not be applied in white bread [75]. Nevertheless, BSG showed a very beneficial impact on the bread protein content due to its composition, increasing it by ~50%, when only 10% of traditional flour was replaced [76]. Combining the protein content with the lack of starch (which is removed during mashing—see Fig. 1), the caloric density of bread containing 10% of BSG may be even 7% lower compared to the conventional bread [77]. Except for the bakery products, brewers' spent grain can be incorporated into other high-fiber foods [78–81]. In general, the food-sector applications of brewers' spent grain were comprehensively discussed in the excellent review works of McCarthy et al. [82], Lynch et al. [48], and lately Rachwał et al. [83].

Energy production Like other types of waste biomass, BSG was also investigated in energy production, which may be implemented within the brewery, leading to reduced production costs [84]. It can be directly combusted. However, it may cause problems related to the high nitrogen content

and resulting generation of nitrogen oxides [85]. Such an effect can be reduced by the application of pyrolysis [86]. Another possibility is converting BSG into charcoal bricks, which increases its calorific value from ~20 to 27 MJ/kg [87, 88]. Multiple works also reported microbial fermentation of brewers' spent grain into bioethanol [89–91] or biogas [92–95], which can be applied as biofuels.

Fermentation Considering fermentation, BSG was investigated as a growth medium [96], e.g., substitute of sucrose or glucose in the lactic fermentation [97–99], medium for pululan production [100], and introduced into manufacturing of xylitol [101–103] or citric acid [104]. The application of wastes and residues for fermentation is a very common and often investigated approach [105].

Among the mentioned fermentation products, lactic acid is an exciting compound for polymer technology. It is commonly applied in poly(lactic acid) manufacturing—one of the most popular biodegradable, thermoplastic polyesters [106]. Over the last years, it attracted much attention due to the application in 3D printing [107]. Moreover, due to the current law regulations, its popularity in manufacturing packaging materials is increasing, often combined with other, less expensive materials like thermoplastic starch [108].

Except for lactic acid, other BSG fermentation products, which could be applied in polymer technology are citric acid [109] and propionic acid [110]. The first one can be applied as a co-monomer in manufacturing of polyesters [111–114] or as a crosslinking agent [115, 116]. Propionic acid is a substrate in the production of polymers based on cellulose derivatives, such as cellulose propionate [117]. Their popularity is growing over the last years due to the current pro-environmental trends related to bio-based polymer materials and their potential novel applications, e.g., in 3D printing [118–120].

Figure 4 summarizes the potential applications of BSG fermentation products in polymer technology. Nevertheless, to the best of our knowledge, no works deal with the application of BSG fermentation products in polymer technology. More details related to the recent developments in the biotechnological valorization of these by-products were presented recently in the comprehensive review work by Puligundla and Mok [121].

Extraction of celluloses and lignin Except for the microbial conversion, various compounds present in BSG, which may find application in polymer technology, can be extracted using different techniques [122–124]. Among the most noticeable components of BSG in terms of polymer technology are celluloses and lignin [125]. They could be applied as fillers for composites and intermediates in manufacturing other raw materials used in polymer technology.



Fig. 4 Potential applications of BSG fermentation products in polymer technology

Mishra et al. [126] presented the multi-stage process of BSG conversion into cellulose nano-fibers consisting of alkali treatments and bleaching. They isolated nanosized fibers with an average diameter of 4.6 nm, shown by atomic force microscopy. Similar fibers are often investigated as fillers for polymer nanocomposites [127–129]. The efficient isolation of fibers and removal of other components of BSG was confirmed by thermogravimetric analysis (lack of decomposition step attributed to the presence of lignin) and X-ray diffractometry (gradual increase in crystallinity index). Similar observations were made by dos Santos et al. [130].

Mussatto et al. [131] investigated the recovery of lignin from BSG. The by-product was subjected to the soda pulping process, comprehensively described in other work [132]. The resulting black liquor was treated with sulfuric acid, which enabled the separation of lignin by precipitation. Except for the lignin, the investigated process enabled the removal of ferulic, *p*-coumaric, *p*-hydroxybenzoic, vanillic, and syringic acids from black liquor. Such an effect points to the presence of these compounds in obtained lignin, which could be applied, e.g., as a filler for wood-polymer composites.

Quite interesting is also the extraction of arabinoxylans from brewers' spent grain. They are hemicelluloses found in plants' primary and secondary cell walls, which consist of copolymers of arabinose and xylose [133]. They play a structural role in plants, and interestingly the significant amounts of phenolic acids are bound to them, so they show noticeable antioxidant activity [134]. Arabinoxylans and their esters

are applied in polymer technology to develop biodegradable and even edible films [135, 136], which could be efficiently applied in food packaging applications [137–139]. They could be enzymatically extracted from BSG in a multi-step procedure [140–142]. The extraction efficiency can be significantly enhanced by the proper particle size distribution of BSG adjusted by milling and sieving, as proven by Reis et al. [143]. Moreirinha et al. [144] used the brewers' spent grain arabinoxylans to prepare composite films with a different share of nanocellulose. Moreover, selected composite films were modified with ferulic acid or feruloylated arabinoxyloligosaccharides obtained from BSG. All prepared films were characterized by the onset of thermal decomposition exceeding typical sterilization or autoclaving temperatures ~ 150 °C. They were characterized by satisfactory mechanical performance, with Young's modulus in the range of 4.3–7.5 GPa (the highest for composite containing 50% of nanocellulose) and tensile strength of 71–110 MPa (the highest for 75% nanocellulose loading). Modifications of films unfavorably affected the mechanical performance but increased the antioxidant activity determined by DPPH assay from the initial 2% to 64–90%. Also, a noticeable reduction in bacterial (*Staphylococcus aureus*) and fungal (*Candida albicans*) growth is beneficial for the potential applications in food packaging.

Extraction of phenolics Except for cellulose, hemicellulose, or lignin, also other compounds can be extracted and isolated from brewers' spent grain. Very auspicious are the phenolics mentioned above, primarily hydroxycinnamic acids, showing antioxidant properties. The BSG should be considered an inexpensive source of these compounds, which could be efficiently applied not only in the food or cosmetic industry [145–147] but also as potential antioxidants for polymer materials [148–150]. Phenolics can be recovered from brewers' spent grain by different variants of extraction, e.g., solid–liquid type or assisted by supercritical fluids, microwaves or ultrasounds, and enzymatic or alkaline reactions [151–153]. As mentioned above, the yield of their recovery strongly depends on the extraction method and its parameters, e.g., selected solvents [154]. Similar phenomena were reported for other by-products, e.g., from the coffee industry, also characterized by high phenolics content [155–157]. The recent advances in the extraction of bioactive compounds, including phenolics, from brewers' spent grain, were comprehensively summarized in the excellent work of Bonifácio-Lopes et al. [158]. Nevertheless, to the best of our knowledge, there are no literature works reporting the application of BSG-originated phenolics in polymer materials.

Liquefaction Considering other, more direct uses of brewers' spent grain in polymer technology, in our previous

work [159], we used the brewers' spent grain as a biomass feedstock for crude glycerol-based microwave liquefaction aimed at manufacturing biopolyols for polyurethanes. The general scheme of the process is presented in Fig. 5. The spectroscopic investigation of obtained polyols revealed that biomass was partially decomposed during the process and reacted with solvent particles. Nevertheless, the efficiency of the process was relatively low, and the hydroxyl values were in the range of 900–1050 mg KOH/g. Such values are very high and could be suitable only for manufacturing very crosslinked and stiff materials. Further studies should include the application of catalysts and optimization of process conditions to enhance its efficiency.

Filler for polymer composites On the other hand, the relatively high fiber content in brewers' spent grain makes it attractive for the preparation of wood-polymer composites, possibly applied in various branches of industry [160]. Other fillers, either conventionally applied wood flour or waste-based, are characterized by a relatively similar composition [161, 162]. Moreover, the presence of proteins, which may act as plasticizers, may facilitate the melt processing of composites [163].

Revert et al. [164] introduced the BSG as a filler into the polypropylene matrix. Nevertheless, due to the polarity differences between filler and matrix, the interfacial interactions were fragile, and the significant deterioration of mechanical performance was noted. The only positive effect of the BSG incorporation was the shift of the oxidation onset temperature attributed to the presence of phenolics showing antioxidant activity. The addition of 10–40 wt% of by-product shifted the oxidation onset by 10–23 °C.

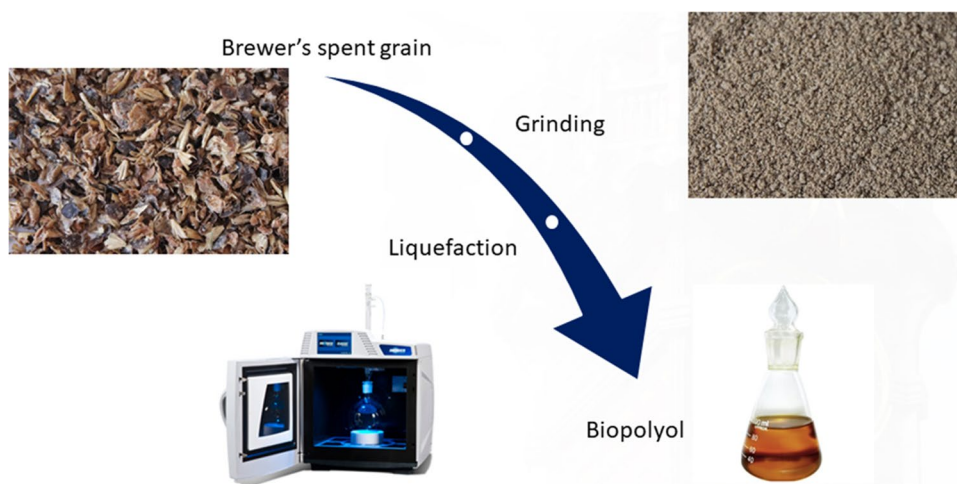
Barbu et al. [165] introduced BSG into particleboards as a partial replacement of wood, which is a common trend in the case of wood-polymer composites [166–168]. The appearance of BSG without additional treatment (presented in Fig. 6) is quite similar to the wood chips, so this

by-product can be easily applied as substitute for conventional raw materials. Particleboards bonded with polymeric 4,4'-methylene diphenyl isocyanate, urea-formaldehyde, or melamine urea-formaldehyde resin. Nevertheless, according to the presented results, to maintain the satisfactory level of the mechanical properties, the content of BSG should be kept at low levels (up to 10%). The structural differences associated with the reduction in particle-particle bonding between wood particles were noted at higher loadings due to the high consumption of glue by BSG. Authors suggested that at higher contents, brewers' spent grain should be combined with innovative glues, based on casein or tannins, which could improve the particle-particle bonding. Similar conclusions about the potential, beneficial share of BSG in wood-based particleboards were provided by Klimek et al. [169], who also suggested the 10% substitution of wood with BSG.



Fig. 6 The appearance of BSG without additional treatment

Fig. 5 The general scheme of microwave-assisted liquefaction of BSG resulting in biopolyol for polyurethanes [159]



A very interesting application of BSG in polymer technology was also presented by Ferreira et al. [170], who used it to prepare disposable trays for food packaging. They were obtained by compression molding of BSG with potato starch applied as a continuous phase. The process was aided with the addition of glycerol, water, and in some cases gelatin, chitosan, or glyoxal applied as crosslinkers. After compression, trays were covered with beeswax. Obtained materials were characterized by significantly higher flexural strength and modulus than commercial trays from expanded polystyrene. Independently of the BSG content (from 20 to 80% in the whole tray), trays showed strength in the range of 1.51–2.62 MPa, compared to the 0.64 MPa for commercial material. Also, the modulus was noticeably higher (1.1–2.0 MPa) compared to polystyrene trays (0.28 MPa). Nevertheless, due to their composition and hydrophilic character of applied raw materials, trays showed significantly higher water absorption than polystyrene, which resulted in a significant 80–90% decrease in mechanical parameters. Such an effect was attributed to the plasticizing effect of water. The application of crosslinkers or beeswax slightly reduced the water absorption. However, deterioration was still noted after immersion, and polystyrene trays showed noticeably superior properties. Nevertheless, presented results indicate that such a solution is quite promising, especially for applications that do not require exceptional resistance to water.

Generally, multiple works dealing with the application of brewers' spent grain in the polymer sector, especially these dealing with its use as a filler for composites or substitute of wood in particleboards, indicate the necessity for modifying this by-product [171, 172]. Modifications should be aimed at enhancing the interfacial interactions with polymer matrices by the change of their hydrophilic character. Such an effect could be achieved by thermo-mechanical treatment resulting in non-enzymatic browning in the caramelization process and mostly Maillard reactions, as presented in our previous works [34, 173]. It is also essential that melanoidins show noticeable antioxidant activity, which can be very beneficial for the oxidative stability of polymer composites [174].

In previous works, we reported the application of thermo-mechanically modified BSG as a potential filler for wood-polymer composites [175, 176].

In the case of poly(ϵ -caprolactone) composites, their mechanical performance was noticeably affected by the parameters of thermo-mechanical treatment of BSG [175]. The increase of modification temperature noticeably affected the interface surface area, resulting in an even 30% increase in composites' toughness. Dynamic mechanical analysis indicated over 30% drop in the adhesion factor and increased the constrained chain volume exceeding 27%. Such an effect points to the significant enhancement of the interfacial interactions.

On the other hand, modified BSG could be effectively applied to substitute traditional wood flour in polyethylene-based composites [176]. Nevertheless, due to the differences in the chemical composition between fillers (presence of proteins, lipids, and melanoidins in BSG, lower content of holocellulose compared to wood flour), the composites' performance was differing. The introduction of BSG resulted in significantly higher values of melt flow index. When wood flour was completely substituted, it increased from 3.23 to 10.56 g/10 min, which was attributed to the drop in viscosity from 1.02 to 0.30 Pa s. A similar effect was noted in our other work [163]. The density and porosity of materials were slightly reduced with the increasing share of BSG due to the presence of proteins, which may enable better encapsulation of filler particles with polymer macromolecules. However, it also caused changes in the composites' mechanical performance. Tensile strength and modulus were reduced by ~27% and ~42%, respectively, but the elongation at break was doubled. Concluding, modified brewers' spent grain could be introduced as partial replacement of conventional wood flour to engineer materials with desired properties.

Others Other, less popular methods of BSG utilization include the manufacturing of adsorbents [177–179], paper [47, 180], bricks [87], or activated carbon [181]. Brewers' spent grain-based adsorbents, and activated carbons were found efficient in the removal of dyes [182–185], volatile organic compounds from the gas phase [186], but mostly metal ions from aqueous media [187–191].

3.2 Trub, spent hops

3.2.1 Overview

Trub is generated during filtration of wort before the fermentation. After cooling down, the wort is separated from the trub, accounting for around 0.2–0.4% of the wort volume [28]. The precipitate contains coagulates of high molecular weight proteins [192]. They are generated during the heat-induced denaturation of proteins. Except for coagulates, the residual hops may be present in trub, because according to the literature data, around 85% of the initial hops mass introduced into wort is removed as a by-product [77]. After extracting the compounds that create the flavor, aroma, and bitterness of the final beer, the solid residues of hops are discarded. However, their content in trub depends on the applied technology of beer hopping [193]. Therefore, the composition of this by-product may be very diverse, depending on the share of coagulates and spent hops.

3.2.2 Composition

Separately, trub contains mostly significant amounts of proteins, even up to 70% of dry matter [83]. Considering spent hops, the proteins account for around 22–23% of dry matter, with a similar share of fiber [194]. According to Mathias et al. [42], around 20% of the residual reducing sugars may also be present in trub. Both trub and spent hops contain relatively low amounts of ash, ~2%, and ~6%, respectively. Interestingly, this by-product may contain noticeable amounts of essential oils and phenolics due to the hop presence. Such an effect is attributed to the low solubility of various compounds in the wort, e.g., in the case of lupulones [195]. On the other hand, phenolics such as hydroxycinnamic acids, gallic acid, catechins, anthocyanidines, and others, are precipitated with proteins and removed as a part of hot trub [196]. The essential oils contain noticeable amounts of terpenes [67]. Moreover, myrcene, alpha-humulene, or beta-caryophyllene are present. They account for ~47% of the essential oil [197]. The structures of main components of essential oils are presented in Fig. 7.

3.2.3 Current applications and potential in polymer technology

Contrary to the brewers' spent grain, the trub and spent hops are significantly less frequently used in animal feeding, despite the beneficial composition, relatively high fiber content, and mostly the presence of proteins. Such an effect is attributed to the presence of hops, particularly bitterness [198]. Another issue is the low energy value of spent hops, which is around 50% lower than spent grains, despite the relatively high fiber content [77]. On the other hand, some research works investigated the combination of spent hops

with other brewery by-products, which resulted in acceptable feed, e.g., for pigs [199]. According to the works of Huszcza et al. [200, 201], the bitter acids originated from spent hops can be removed or degraded by yeast or fungi. More recent works dealing with the trub and spent hops investigated the reduction of bitterness by the multi-step extraction of bitter compounds [202]. During extraction, most carbohydrates were removed together with tannins and phenolics, which are often bound to the carbohydrates. As a result, the share of proteins and fat was increased from the initial 26.5% and 5.2% to 70.3% and 9.9%, respectively. Due to the significant drop of phenolics content (from ~350 to ~125 mg gallic acid equivalents/100 g), the antioxidant activity was also noticeably reduced. Nevertheless, changes resulting from the extraction allowed the use of modified trub in food applications.

Considering the most popular uses of biomass and brewery by-products, except for the animal feed, trub and spent hops may be applied as a soil conditioner and fertilizer, which is associated with their high nitrogen content [42, 203].

As mentioned above, the trub and spent hops contain noticeable amounts of essential oils and phenolics. These compounds can be effectively extracted from this by-product and potentially applied in polymer technology. Bedini et al. [197] reported that the terpenes present in spent hops could be applied as the repellents against the insects, e.g., *Rhyzopertha dominica* or *Sitophilus granarius*. Spent hops essential oils were 2–5 times more effective against *R. dominica* than *Laurus nobilis* oils [204] and showed similar repellency against *S. granarius* as *Hyptis suaveolens* oils [205]. Bartmańska et al. [206] also showed antifungal activity of spent hops extracts against *Botrytis cinerea*, *Fusarium oxysporum*, *Fusarium culmorum*, and *Fusarium semitectum*. Therefore, the application of spent hops or only their essential oils in manufacturing the packaging materials seems reasonable. The extraction and isolation of essential oils from spent hops can be performed by hydrolysis, steam distillation, but also using supercritical CO₂ or eutectic solvents [207–210].

Moreover, this by-product can be applied in fermentation processes as a supplement for microbes due to the high nitrogen content [83] and the presence of lipids and zinc [211].

3.3 Spent yeast

3.3.1 Overview

During the initial stage of fermentation, the intensive proliferation of yeast is occurring, so after fermentation and maturation, the surplus of yeast is present and should be removed from beer [212]. Partially, they are recovered by natural sedimentation, but for higher efficiency, additional

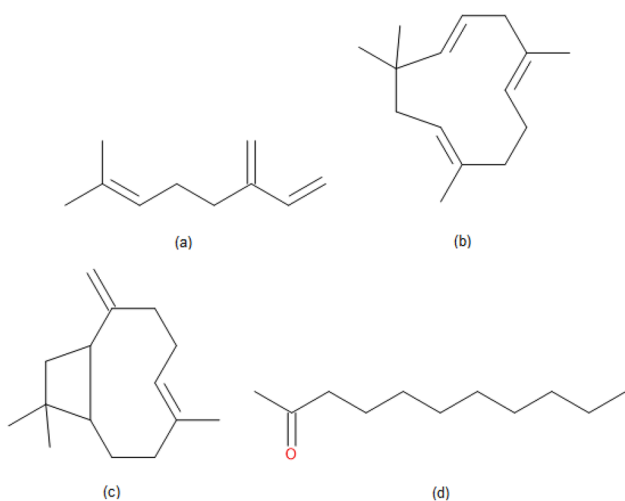


Fig. 7 The main components of spent hops essential oil: **a** myrcene, **b** α -humulene, **c** β -caryophyllene, and **d** 2-undecanone [197]

filtration or centrifugation may be applied [213]. The actual amount of this by-product depends on the type of yeast used for fermentation, but it can account even for 15% of total by-products generated during beer production [214]. Around 0.3 kg of spent yeast is generated per hectoliter of beer. Depending on the properties of yeast, in particular their flocculation, this by-product is characterized by the high moisture content in the range of 75–90%. Therefore, portion of beer is removed along with yeast, which may generate the 1.5–3.0% loss of beer [28].

3.4 Composition

Considering the composition, spent yeast contains a noticeable amount of carbohydrates and proteins. Among the first group, the most abundant are non-cellulose compounds (25–35%), mainly β -glucans, mannoproteins, and glycogen, followed by cellulose (17–25%) [215]. Proteins may account for more than 50% of the spent yeast dry mass [195, 216]. Jacob et al. [217] reported even value of 74.3 wt%. Therefore, the spent yeast is characterized by the lowest carbon:nitrogen ratio among the brewing by-products, around 5 [42]. Literature works report different amino acid compositions of spent yeast. According to Vieira et al. [218], the most common amino acids in spent yeast are alanine (even over 9%), arginine, aspartic acid, and cysteine. At the same time, Jaeger et al. [219] indicated that glutamic acid is the most abundant one (~15%), followed by histidine, alanine, arginine, and aspartic acid. Such an effect may be associated with the differences between particular *Saccharomyces cerevisiae* strains applied worldwide [220].

Brewery spent yeast are also a great source of micro- and macroelements, as well as vitamins. Nevertheless, the mineral composition of yeast can differ depending on the length of fermentation and fermentation cycles [67]. Among the most abundant minerals are sodium, potassium, and magnesium, but noticeable amounts of phosphorous may be present, which could be associated with yeast nutrients in breweries [195]. Considering the vitamins, the B type is the most popular, especially niacin, thiamin, pantothenate, and riboflavin [218].

3.4.1 Current applications and potential in polymer technology

Due to the high content of proteins, vitamins, and minerals, the spent yeast is mostly applied as an additive in animal feeding [221]. It has been repeatedly proven that such application of this by-product shows very positive effects on the animals' health. It may result in increased milk production, improved microflora, and enhanced resistance to various microorganisms [222–224]. Except for the animal feed, spent yeast was also investigated in human

consumption. However, they show great potential due to the high contents of nucleic acids (6–15%), in particular ribonucleic acid, their use in an unmodified state is somewhat limited [216]. The ribonucleic acid is metabolized to the uric acid in the human body, which can cause gout [225]. Generally, the spent yeast application in animal and human nutrition was comprehensively discussed in dedicated review works [219, 226–229].

Another broadly investigated application of spent yeast is cultivating microorganisms and other biotechnological processes [230, 231]. Due to the beneficial composition of brewery spent yeast, various microorganisms cultivated on this by-product may grow noticeably faster than other yeast types, as reported by Ferreira et al. [232]. As a result, the spent yeast may be applied as a very efficient source of multiple enzymes, including proteinases [233], proteases [234, 235], or pectinases [236, 237]. Moreover, brewery spent yeast can be applied as nutrients during ethanol or lactic acid fermentation [238, 239]. Pietrzak and Kawarygielska [240] showed that the 5% addition of brewery spent yeast might increase the rate of sugar consumption and ethanol production resulting in even 11% enhancement of ethanol yield. Such an effect was ascribed to the high nitrogen content of the medium.

Other, less popular uses of spent yeast from beer production include methane production or application as biosorbent. Considering the energy production, spent yeast can be considered an excellent substrate for co-digestion purposes with other materials, including swine manure [241], spent grains [242], or crude glycerol [243].

Considering the polymer technology point of view, the brewery spent yeast show hardly any applications. The most promising and the closest to polymer technology is their use in fermentation processes generating lactic or succinic acid. The use of lactic acid in polymer technology was described in Sect. 3.1.3. The succinic acid can be applied in the manufacturing of polyesters or alkyd resins [244, 245].

Rakin et al. [246] reported that the application of spent yeast might increase the rate and yield of lactic acid fermentation due to the presence of amino acids, vitamins, and minerals. Similar observations were made by Champagne et al. [247]. According to Radosavljević et al. [248], the brewery spent yeast, combined even with other brewery by-products, can act as a low-cost fermentation medium for manufacturing of lactic acid.

Considering succinic acid production, the substitution of conventional yeast extracts with hydrolysate of spent brewery yeast as a nitrogen source was successfully achieved by Jiang et al. [249] and Chen et al. [250].

Nevertheless, to the best of our knowledge, there are no literature reports directly connecting the brewery spent yeast with the polymer technology.

4 Conclusions, future trends, and developments

The presented review summarized the literature works associated with the by-products of beer production. Their generation during brewing was discussed, and the beer market size, which affects the amount of by-products. Reported data about the composition of brewers' spent grain, trub, spent hops, and spent yeast indicate that the application in polymer technology should be considered an auspicious method of their utilization, viable from the ecological and economic point of view. Moreover, their chemical composition, particularly the presence of compounds showing antimicrobial, antifungal and antioxidant activity, puts the brewing by-products as potential active fillers providing additional properties to polymer materials and promising intermediates in manufacturing various raw materials for polymer technology.

In order to take full advantage of the brewing by-products potential in polymer technology, future works should focus on the following issues:

- Partial substitution of conventional lignocellulosic fillers in wood-polymer composites with brewers' spent grain, which could enhance the resistance to thermooxidation.
- Investigations related to the mechanisms of the enhancement of thermooxidative stability of various polymer materials by antioxidants present in brewing by-products.
- The applications of brewing by-products in packaging materials or even edible films for food protection.
- Liquefaction of brewing by-products resulting in raw materials for manufacturing of polyurethanes or polyester resins.

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Declarations

Competing interest The author declares no competing interests.

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