Chapter 7

Exploitation of Brewing Industry Wastes to Produce Functional Ingredients

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Abstract

Nowadays, the consumers' global demand for healthier diets is steadily increasing, and the development of novel functional ingredients has become a focus of the food industry. On the other hand, the accumulation of huge amounts of food wastes every year has led to environmental degradation and especially to significant loss of valuable material that could otherwise be exploited as new health-promoting ingredients, fuels and a great variety of additives. In this respect, the biggest challenge of the current scientific world is to convert the underutilised by-products generated by the food and beverage industries into more profitable and marketable added value products which would also contribute significantly to meet the nowadays society needs. This chapter gives an overview regarding the possibility of exploiting the brewing industry wastes as sources of bioactive compounds in order to produce functional ingredients and products with added value.

Keywords: brewing wastes, bioactive compounds, innovative functional ingredients, waste management, complete valorisation

1. Introduction

The research on the recovery of new functional ingredients from natural sources is one of the most important challenges in food science and technology [1, 2]. In recent years, it has been noticed a significant increase in the number of research providing scientific evidence to support the hypotheses that phytochemicals recovered from agro-industrial wastes can provide a range of health benefits to the consumers. This fact has impacted the food and pharmaceutical industries, among

others. The phytochemical extracts can be used either for their biological properties as ingredients for nutraceutical preparations or functional foods or for their food-quality-related properties [3].

In the food industry, the traditional significance of "processing" is associated with transformation of the initial raw material into a safe, nutritious and high-quality food product. However, in a modern bio-based society, food processing should also provide viable alternative models that combine food production with valorisation of waste and by-product, minimisation of energy consumption and environmental protection [4].

The brewing industries produce millions of tons of residues, which represent a management issue from both ecological and economical point of view. The accumulation of huge amounts of this biomass every year leads to environmental degradation and especially to significant loss of valuable material that could otherwise be exploited as food, fuels and a great variety of additives. The valorisation of brewing by-products can be achieved through the extraction of high-value components such as proteins, polysaccharides, fibres, flavour compounds and phytochemicals, which can be reused as nutritionally and pharmacologically functional ingredients [5–9]. Nowadays, the advances in scientific research support the idea that diet may fulfil nutritional needs and at the same time exert a beneficial role in protecting the human body of some diseases. The idea of health-promoting foods is not new: Hippocrates wrote 2400 years ago, "Let food be thy medicine and medicine be thy food." Thus, the production and consumption of functional foods have gained much importance as they provide a health benefit beyond the basic nutritional functions [10, 11]. The innovative approach in developing a new generation of functional ingredient and foods is focused on finding unconventional sources of bioactive compounds and optimising the most appropriate recovery system.

In this chapter, we will address the exploitation of brewing-derived by-products as sources of bioactive compounds and functional ingredients.

2. Bioactive compounds recovered from brewing wastes and their potential applications as functional ingredients

2.1. General overview

The recovery and reuse of the brewing industry by-products to extract functional compounds and develop new innovative products are a research direction of great interest and actuality from the perspective of food—health relation as well as from the environment protection and waste management perspective.

During production, beer alternately goes through three chemical and biochemical reactions: mashing, boiling and fermentation. In the mashing stage, malt starch is converted to fermentable sugars (mainly maltose and maltotriose) and non-fermentable sugars (dextrins), and proteins are partially degraded to polypeptides and amino acids. This enzymatic conversion stage produces sweet liquid called wort and a residual solid fraction called spent grains. After filtration, the wort is transferred to the brewing kettle where it is boiled with the addition of hops. During this process, the bitter and aromatic hop components will confer typical beer qualities, such as bitter

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taste, flavour and foam stability. At the boiling end, the liquid extract is separated from the spent hops to be further processed. A fraction of the hop components end up in the trub (a precipitation product of the wort boiling process that may include insoluble hop materials, condensation products of hop polyphenols and wort proteins, and isomerised hop acids). During fermentation, the yeast cells will convert the fermentable sugars to ethanol and carbon dioxide. At the end of this stage, most of the cells are collected as spent yeast [7, 12, 13]. According to the technological process shown schematically in **Figure 1**, the main by-products generated in the brewing process are spent grain, spent hops and trub and spent yeast.

There is a wide range of extraction techniques used for the isolation and purification of the bioactive compounds from brewing wastes, some of them based on new emerging techniques. The extraction of the high-value components must be economically feasible to perform. This objective can be achieved by separating the components of interests through individual and/or combined physical and biochemical approaches in order to provide a range of components, all of which would contribute to achieving whole-waste exploitation [6, 9]. The extraction conditions are extremely important, due to their effects on the release of compounds from the matrix into the medium and also due to structural changes that may occur and alter the expected properties. Thus, the optimisation of the existing methodologies and development of new extraction methods to increase the extraction yield, the selectivity for a certain compound, to protect their functionality or to extend the applicability in the food industry are of utmost importance. Also, in order to increase the overall sustainability of the reuse

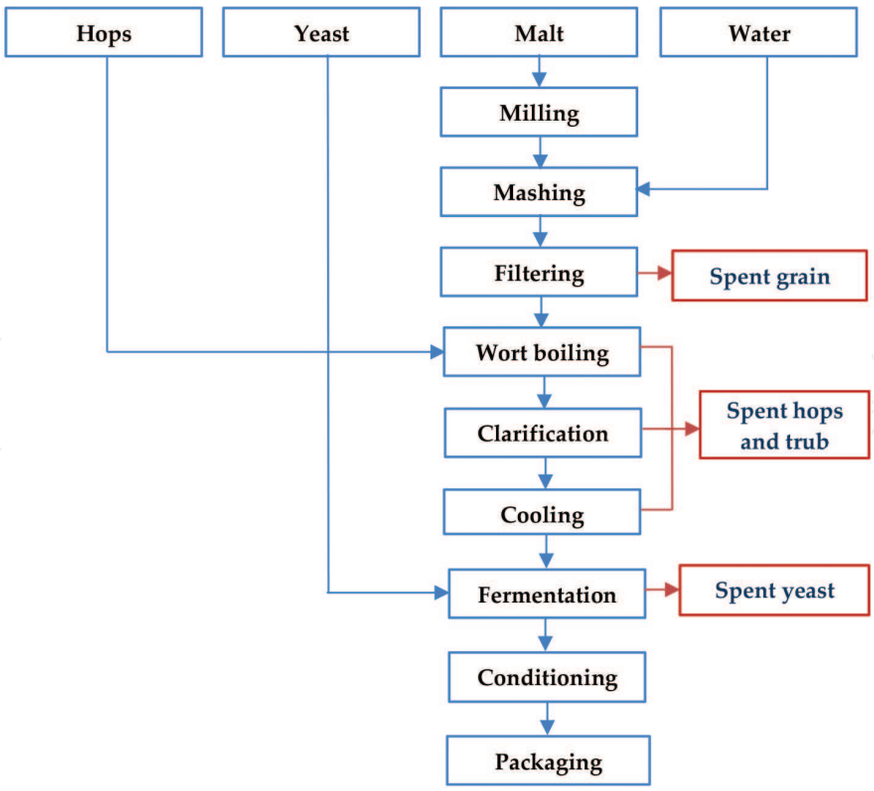

Figure 1. Schematic representation of the brewing process and points where the main by-products are generated.

of components of by-products in food life cycle, it will be necessary to apply and promote novel eco-friendly extraction technologies capable of reducing the solvent consumption and to ensure the environmental protection [6, 14, 15].

2.2. Brewers' spent grain

The brewers' spent grain (BSG) is the main solid waste produced in large quantities by the beer industry, resulted after mashing and filtration stage. This insoluble material basically consists of the barley grain husk in the greatest proportion, minor fractions of pericarp and fragments of endosperm and other residual compounds not converted into fermentable sugars by the mashing process [8, 16, 17].

2.2.1. General characterisation of BSG

In the brewery, the malted barley is milled and mixed with water in the mash tun, and the temperature of mash is slowly increased from 37 to 78°C in order to promote the enzymatic conversion of malt constituents. After the saccharification process, the clear sweet wort is separated from the solid components—the spent grain. The wort is then transferred to the wort kettle, whereas the spent grain is removed from the lauter tun [18].

As described in the literature, the chemical composition of BSG is variable according to the barley variety and harvest time, malting and mashing conditions, type and quality of secondary raw materials added in the brewing process. A major influence is that different barley cultivars are used as the malt source for lager and ale beer. In general, ale malt is kilned at a higher temperature, whereas lager malts are derived from barley with higher protein content [8, 12, 19, 20]. Recent research on the evaluation of the BSG biomass showed surprising results both in terms of the variety of classes of compounds and the quantity of the functional part. Even if BSG chemical composition is dependent on the intrinsic and extrinsic factors mentioned above, it contains appreciable amounts of valuable compounds (proteins, lipids, carbohydrates, polyphenols, minerals) that remain unexploited in the brewing process [5, 7, 8, 17].

BSG is an important by-product from the brewing process, representing up to 30% (w/w) of the starting malted grain. It is estimated that worldwide the annual output is around 30 million tons, about 200 tons of wet BSG (70–80% water content) being produced per 10.000 hl of beer. Traditionally, this material is sold as animal feed or discarded [8, 16, 21, 22]. Due to the significant amount produced annually, the low market value, environmental awareness and the recognition that BSG may represent a nutritionally valuable co-product, efforts should be increasingly focused on its valorisation [17, 23, 24].

The high initial water content of fresh BSG (75–80%) and the presence of considerable levels of polysaccharide, residual fermentable sugars and proteins make BSG very susceptible to microbial degradation within a few days [25]. Microbiological stabilisation is an imperative that should be designed into BSG processing systems in order to avoid the growth of microorganisms. The implications for microbiological spoilage by a resident microflora might affect also the potential to use BSG as a reliable food-grade industrial feedstock for value-added

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downstream processing [20]. One of the most common and economically feasible methods used for preservation is the drying of BSG, thus reducing the water content and lowering the microbiological activity. This preservation method is also interesting in terms of reducing the volume of the product and, therefore, decreasing transport and storage costs (**Figure 2**) [19].

2.2.2. Bioactive compounds and potential applications

2.2.2.1. Proteins and amino acids

The protein content of barley varies from 8 to 15%. During malting, barley proteins are partially degraded to amino acids and small peptides by the endogenous barley peptidases. However, most of malt proteins are not dissolved in mashing but 74–78% of protein remains insoluble in the spent grains. As a result, BSG has a high content (18–35.4%, w/w) of quality protein [16, 26–28]. For a by-product to be considered as a source of quality protein, it must contain a well-balanced essential amino acid composition [9, 29]. In BSG, the essential amino acids represent approximately 30% of the total protein content. Lysine, known to be the limiting amino acid in cereal derived foods, accounts for 14.3% of the total BSG protein content. Other amino acids in significant quantity are: leucine, phenylalanine, isoleucine, threonine and tryptophan [21]. Depending on the raw materials used in brewing process (unmalted grain, corn, barley, wheat, rice), protein composition can vary significantly thereby modifying the essential amino acids profile of BSG. Owing to its protein-rich composition, BSG has the potential to be utilised in a manner similar to whey protein, providing health benefits for consumers [7, 21, 30, 31]. Essential amino acids of BSG derived from 100% barley malt expressed as a percentage of total protein [21] are listed in **Table 1**.

The lack of solubility of BSG proteins presents a barrier for their more extensive use in food processes and products. Protein hydrolysates from agricultural crops have already demonstrated bioactive effects which support their potential use as functional food ingredients. In addition, these products can have numerous properties indispensable for the food industry such as emulsifying agents, film forming properties, flavour binding, viscosity increase by

Figure 2. Fresh (left) and dried (right) BSG.

Essential amino acids (% of total protein)	Barley	Malt	BSG
Lysine	2.52	3.69	14.31
Leucine	0.30	0.29	6.12
Phenylalanine	0.20	0.21	4.64
Isoleucine	0.17	0.17	3.31
Threonine	0.01	0.02	0.71
Tryptophan	0.01	nd	0.14

Table 1. Essential amino acids content of BSG derived from 100% barley malt.

binding the water and gelation properties. To expand the potential applications of insoluble proteins, chemical and enzymatic hydrolysis can be applied [16, 27, 32]. However, BSG protein fraction can be a valuable substrate for enzymatic hydrolysis to produce hydrolysates with biological properties. BSG protein hydrolysates are also of high importance when considering incorporation into food products, particularly with respect to their techno-functional properties, of which solubility, emulsifying properties, immune-modulatory effects and antimicrobial activity are very important. Protein hydrolysis changes the molecular weight, charge and exposure of hydrophobic groups and amino acid side chains, which alters solubility, viscosity, sensory properties and emulsifying and foaming behaviour [17, 21, 27, 33–35].

In the present, studies have already demonstrated that food with incorporated protein hydrolysates derived from BSG possesses anti-inflammatory activity [32, 36]. Moreover, the incorporation of chitosan into the brewers' spent grain protein had as result a composite film with antimicrobial and antioxidant activities which can be used in packaging materials [34].

2.2.2.2. Polysaccharides

The main constituents of BSG include fibres and proteins, which are staple nutritional components in the human diet and thus make this material very attractive for improving the nutritional value of foods. In addition, several components that are constituents of BSG, such as arabinoxylans, β-glucans and phenolic compounds (e.g. hydroxycinnamic acid), have gained increasing attention due to their potential health benefits. The determination of the beneficial implications of dietary fibre in a wide variety of food products has resulted in fibre being regarded as a "functional" ingredient. The physiological responses to fibre consumption have been well documented in relation to reduced risks of chronic diseases [37]. BSG contains the husk and the outer layers of the barley kernel thus being a heterogeneous material rich in arabinoxylan (22 − 28%), cellulose (17 − 25%) and lignin (12–28%). This lignocellulosic material is constituted by several polysaccharides, which can be degraded into their corresponding constituents by hydrolytic procedures (hydrothermal, enzymatic or acidic). On hydrolysis, cellulose yields glucose, whereas the hemicellulose yields xylose, arabinose, mannose, galactose and the acids, acetic and hydroxycinnamic (ferulic and p-coumaric) [13, 22, 38]. The released monosaccharides can be further subjected to a fermentation process to generate valuable products

(e.g. xylitol, a healthy sweetener used in food industry) [39]. Also, the arabinoxylans are considered dietary fibres with a broad range of potential uses as functional ingredients in food products. In addition, for maximising the valorisation efficiency of BSG, an innovative integrated process that sequentially extracts the proteins and arabinoxylans was recently developed [16].

An alternative of reuse of dried BSG is as flour incorporated in food products [19, 28]. Fibre is suitable in meat products because it retains water, decreases cooking losses and has a neutral flavour. Therefore, having a high potential as a source of dietary fibre BSG can be used as a fat substitute for producing high-dietary fibre and low-fat meat products, reduces the number of synthetic antioxidants needed to be added and increases the health-promoting properties of the frankfurters [37]. Also, BSG was successfully used in smoked sausages meat products to partially replace the animal protein [40]. Processing BSG into flour represents a viable alternative for its use as a functional ingredient in bakery products. Different percent of BSG flour added to bakery products resulted in increase of total dietary fibre, total protein content, lipids, minerals and water holding capacity of the final product. The substitution of wheat flour with 5–20% BSG resulted in bread prototypes with enhance nutritional value and with pleasant flavour characteristics imparted by the specific volatile compounds [19, 21, 28, 41–43].

Recently, BSG was investigated as potential raw material for cellulose nanofibre production. Anticipated applications of nanocellulose range from food (e.g. emulsion/dispersion) to medical, cosmetic, pharmaceutical, hygiene/absorbent products and even usage in various nanocomposites and paper applications [44–46].

Due to the composition rich in sugars and nutritional factors, hydrolysates produced from BSG can be used in fermentative processes to produce several compounds of industrial interest. The BSG biomass can also be exploited by microbial-processing in order to obtain valuable enzymes and organic acids. These valuable chemicals can be further exploited as raw materials for other processes or as functional ingredients for development of new generations of added-value food products and not only. Some examples include the use of the sugar rich hydrolysate as fermentation medium for the production of ethanol by *Saccharomyces cerevisiae*, xylitol by *Candida guilliermondii*, xylitol, arabitol, ethanol and glycerol by *Debaryomyces hansenii*, and lactic acid by *Lactobacillus delbrueckii*, *Lactobacillus pentosus* or *Lactobacillus rhamnosus* [13, 47, 48].

2.2.2.3. Phenolic compounds

The recent worldwide tendency to avoid or at least decrease the use of synthetic additives has created a need for alternative cheap, renewable, natural and possibly safer sources of natural compounds with antioxidant and antimicrobial activities to stabilise foods against oxidative rancidity and microbial spoilage [49]. Having strong antioxidant activity, when ingested, the antioxidants protect the human body from the damaging actions of the reactive oxygen species and thus lowering the risk of several chronic diseases (cardiovascular diseases, diabetes, cancer) [7, 9, 33, 50, 51].

Beer contains a large variety of phenolic components derived from the biotechnological fermentation of barley malt (70%) and hops (30%) that are responsible for the overall antioxidant

activity of the beverage. These compounds play an important role in flavour, colour and shelf life of beer [52]. Since most of the phenolic compounds of the barley grain are contained in the husk and hydroxycinnamic acids accumulate in the cell walls, BSG is a potentially valuable and inexpensive source of phenolic acids. Ferulic acid (1860–1948 mg/g) and p-coumaric (565–794 mg g^{-1}) are the most abundant phenolic acids in BSG, followed by sinapic, caffeic and syringic acids [7, 9, 17, 33]. The content in polyphenols is influenced not only by the extraction technique but also by factors such as barley cultivar, malting conditions and the presence or absence of the hull. Depending on the solvent used for extraction, studies reported for total phenols in BSG values ranging from 2.14 to 9.90 mg GAE/g and a flavonoid content varying between 0.02 and 4.61 mg QE/g [50]. **Table 2** overviews the results of the authors' own research regarding the total phenols, flavonoids and radical scavenging activity values for barley, malt and BSG samples.

However, the application of BSG to food is still limited, since it can impart unpleasant flavours and aromas. This negative effect was associated with high quantities of compounds such as 2-butyl-1-octanol, 3-methyl-butanal, 2-heptane, butanal, benzene and 2, 3-butanedione, responsible for its characteristic unpleasant odour [53]. In a recent study, the polyphenols and flavonoids compounds extracted by supercritical CO_2 from BSG were microencapsulated to mask their unpleasant and bitter taste and simultaneously to preserve the stability of polyphenols or other bioactive compounds. The tests on fish-burger formulation with microencapsulated polyphenols showed to have about 30% of phenolic and about 50% of flavonoid content more than the control sample and a better antioxidant activity [53].

2.2.2.4. Lipids and fatty acids

Another important BSG macro-nutrient includes lipids and fatty acids. The high amounts of lipids in BSG make this material an interesting feedstock for the production of high value-added lipids in the context of the so-called lignocellulose biorefinery [5]. The lipids in barley are located in the endosperm and embryo, as their role is to provide nutrients and energy for the new, germinating barley plant. Although the endosperm is almost completely solubilised in mashing, most of the lipids remain with spent grains and are not transferred to wort [54–56]. According to recent studies [5, 8, 55, 57], the total lipid contents (TLs) of BSG

Sample	Total phenols (mg GAE/100 g fw)	Flavonoids (mg QE/100 g fw)	DPPH inhibition (%)
Barley	133.93	6.17	43.17
Pilsner malt	148.42	5.28	46.36
Caramunich malt	256.42	10.72	57.87
Carafa malt	335.88	8.97	42.07
Dried BSG	284.20	13.16	55.95
Lyophilised BSG	291.47	10.35	53.78

Table 2. Total phenols, flavonoids and radical scavenging activity values for barley, malt and BSG.

varied between 5.40 and 11.00% (dry-mass). Only minor changes in fatty acid composition occur during malting and mashing, and therefore, the fatty acid composition of BSG is similar to that of barley [8, 54].The predominant lipid classes identified in the total lipids of BSG were triacylglycerols (TAG) (55–67% total lipids), followed by free fatty acids (FFA) (18–30%), diacylglycerols (DAG) (7.7–5.7%), monoacylglycerols (MAG) (1.7%), phospholipids (PL) (9.1%) and steroid compounds (SC) (hydrocarbons, ketones, free sterols, sterol esters and sterol glycosides) (5%) [5, 55]. The high amount of free fatty acids in BSG can be attributed to the endogenous lipase that is able to release the free fatty acids from triacylglycerols and polar lipids during malting and mashing [5, 55]. **Table 3** contains the results of the authors' own research regarding the fatty acids profile of barley, malt and BSG [8].

Regarding the fatty acids composition (GC-MS analysis) of lipids from BSG, the studies showed that the most abundant was linoleic acid (18:2, *n*−6) that accounted for 50–51.50% of all identified fatty acids, followed by palmitic (16:0) (25–26% of total fatty acids) and oleic acids (18:1, *n*−9) (12–13% of total fatty acids). Small amounts of other fatty acids, such as stearic (18:0) and linolenic (18:3, *n*−3) acids, were also reported [8, 55]. The elevated level of linoleic acid (18:2, *n*−6) from the BSG lipids is comparable to those of "linoleic acid-rich" vegetable oils, such as grape seed, hemp seed and wheat germ oils [58]. This acid is an *n*−6 essential fatty acid, which can be used in pharmaceutical and cosmetic products, and is considered to influence the metabolic processes in the skin and to promote the activity of different lipophilic vitamins, such as A and E [5].

2.3. Brewers' spent yeast

The brewers' spent yeast (BSY) is another brewing by-product that merits considerable attention, due to the large quantity produced (is the second largest by-product from breweries) and its rich chemical composition.

Fatty acids (% of total fatty acids)	Barley	Pilsner malt	Caramunich malt	Carafa malt	Dried BSG
∑SFAs	24.57	25.87	23.68	25.90	29.78
∑MUFAs	17.36	14.26	17.25	18.23	14.53
∑PUFAs	58.07	59.86	59.07	55.87	55.69
∑*n*−3 PUFAs	4.82	5.11	5.78	4.37	5.18
∑*n*−6 PUFAs	53.25	54.75	53.29	51.50	50.51
n−6/*n*−3	11.04	10.71	9.22	11.78	9.75
PUFAs/SFAs	2.36	2.31	2.49	2.16	1.87
∑VLCSFA (≥20 C)	0.89	1.01	0.63	0.62	0.96
Total lipids (% of dw)	2.96	2.55	2.31	2.74	6.61

SFAs, saturated fatty acids; MUFAs, monounsaturated fatty acids; PUFAs, polyunsaturated fatty acids and VLCSFAs, very long-chain saturated fatty acids.

Table 3. Total lipids composition and the major lipid fractions from barley, malt and BSG samples analysed by GC-MS.

2.3.1. General characterisation of BSY

Brewing yeast *Saccharomyces cerevisiae* is the technological biocatalyst, which produces beer from fermentable substrate by alcoholic fermentation. After 10–15 successive fermentation batches, the yeast, due to increasing contamination, loses its viability and vitality and is no longer proper for making beer [59]. BSY is the second major by-product of the brewing industry with environmental impact due to the disposal of a large quantity of biomass (1 hl of beer generates 2.0–4.0 kg of BSY) [60, 61]. BSYS can be collected from fermentation and storage tanks, the yeast storage plant and from the filter line. The quantity and quality of biomass harvest at the end of brewing production depend on the pitching rate, the yeast viability, the yeast strain, the purity of the yeast culture, the wort composition, the particulate content of the wort, the timing and extent of wort aeration/oxygenation, the fermentation conditions and the plant capability [62]. Management of BSY is one of the most important concerns of breweries. BSY contains liquids in large quantities (85–90%), which makes handling and disposal difficult and expensive. As a good practice, the brewers concentrate the waste yeast (to 22–25% dry matter) and also recover the beer to reduce losses [25, 63, 64].

2.3.2. Bioactive compounds and potential applications of BSY

The major chemical compounds of BSY are represented by carbohydrates, proteins, free amino acids, ash, vitamins and fatty acids. The predominant amino acids found in brewer's spent yeast proteins are leucine, lysine, tyrosine, arginine, cysteine, histidine, isoleucine, methionine, phenylalanine, threonine, tryptophan and valine. Thus, BSY is an excellent source of high-quality protein, comparable in value with soy protein. Also, reported high values of glutamic acid and glutamine contents, increase the potential use of BSY extract in food industry as a "hidden ingredient" of natural monosodium glutamate, which is known to provide the typical"umami" aroma, very similar to meat aroma [25, 65, 66]. The inner layer of the BSY cell wall contains β-glucans 8% (w/w dry weight), and the external layer is formed by mannoproteins [67]. These two classes of compounds have immunomodulatory, antimutagenic and anticarcinogenic activities, being also utilised in cosmetic products, and lately in food industry as natural emulsifiers [68–70]. The physicochemical properties of β-glucans depend on the characteristics of their primary structure, including linkage type, degree of branching, molecular weight and conformation. β-glucans from yeast, which consist of a (1, 3)-β-linked backbone with small numbers of (1, 6)-β-linked side chains, are essentially known for their immune-modulating effects [71, 72]. They also stimulate the skin cell response to combat free radicals thus significantly delaying ageing process. The European Food Safety Authority (EFSA) has already approved the use of *Saccharomyces* β-glucans as a new food ingredient and suggests a use ranging between 50 and 200 mg per serving [73]. β-glucans from BSY have potential applications in food industry as food thickeners, fat replacer, dietary fibres, viscosity imparting agents, emulsifiers and films [74]. For example, due to its lower calories content, BSY can be a valuable source of cheap easily assailable fibre, with recently proved prebiotic effect, which makes it of interest for pastry industry, in order to develop value added products [66, 75].

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Nevertheless, BSY has a strong antioxidant activity, comparable with that of teas, due to phenolic compounds adsorbed from malt and hop in the brewing process. BSY contain a high level of phenolic compounds in both the free and bounded forms: gallic acid, protocatechuic acid, (±) catechin, p-coumaric, ferulic and cinnamic acids, which makes BSY a potential functional ingredient [76, 77].

Other compounds derived from hops include α- and β- acids, which have a strong antimicrobial activity [78]. The α-acid content ranges between 167 and 2074 μg/g, with an average related to the total hop acid between 487 and 2557 μg/g. When centrifugation is used for yeast separation, the amount of hop acids is higher, demonstrating the BSY affinity for these compounds [79].

The lipid fraction of the BSY accounted for 4.4% of dry biomass, 58% of which were neutral lipids. Mono-, di- and triacylglycerols, squalene, lanosterol, ergosterol, steryl esters and free fatty acids were identified in the neutral lipid fraction. Although brewers' yeast does not belong to the so-called lipid yeasts, the high content of squalene gives reason for additional exploitation of this by-product [80].

BSY consumption as protein source for human nutrition is limited by the high level of nucleic acids (6–15%) which can cause increase in the level of uric acid in the blood and tissues. This restricts the use of BSY to the status of a dietary supplement as powders, flakes, tablets or in liquid form, rich in bioactive compounds: vitamins, especially B vitamins and minerals (calcium, phosphorus, potassium, magnesium, copper, iron, zinc, manganese, selenium and chromium). In order to be used as dietary supplement, BSY has to be subjected to a debittering process that can conventionally be achieved by washing with an alkaline aqueous solution or by water vapour distillation with or without an organic solvent treatment [81, 82].

Autolysed BSY extract occurs by the natural action of endogenous enzymes when cells complete their growth cycle. The cell wall gets disrupted as the yeast's enzymes break down proteins, releasing amino acids, salts and carbohydrates. The soluble portions are separated from the insoluble components by centrifugation and several filtration steps, including ultrafiltration. The final product is either stored in liquid or paste form or may be spray-dried to a powder [25, 63]. BSY hydrolysates are obtained by acidic or enzymatic (proteolytic enzymes) hydrolysis. The BSY extracts manufactured by autolysis and hydrolysis are used as a functional ingredient in a variety of processed foods: meat paste, soups, sauces, snacks and vegetarian foods, but due to the high salt content, it may have limited uses [83].

Yeast extract from BSY could be used in a large variety of food as flavour enhancers [63, 84]. The intracellular enzymes nucleases produce nucleotides and nucleosides, of which 5′-guanosine monophosphate and 5′-inosine monophosphate act as flavour enhancing—the so-called umami effect proteases breakdown the proteins into smaller polypeptides and sulphur amino acids that provide komumi taste, continuity, mouthfulness and thick flavour. Several sulphur-containing compounds, identified as S-allyl-cysteine sulphoxide (alliin) and glutathione (GSH, γ-Glu-Cys-Gly), were responsible for this effect [85].

2.4. Brewers' spent hops and trub

Only 15% of the hops constituents will be retrieved in the beer, whereas 85% will become spent hop material. A fraction of the hop components will end up in the trub, mainly when hop powdered pellets or extracts are used in the brewing process. The hot trub is a precipitation product of the wort boiling process that includes: insoluble hop materials, condensation products of hop polyphenols and wort proteins and isomerised hop acids adsorbed on the trub solids [12, 13]. Compared to BSG, the direct use of spent hops as feed supplement is not desirable due to the presence of 2-methyl-3-buten-2-ol, which is the product of bitter acid degradation and has hypnotic-sedative properties. Traditionally, spent hops have been used as a fertiliser and soil conditioner, due to the high nitrogen content or mixed with spent grain and sent to animal feeding. However, there are several compounds can be recovered from spent hops, such as flavours, saccharides and organic acids, which can be obtained after oxidation or hydrolysis of this material. Among these compounds, the hop acids, particularly, have antibacterial potential being a safe alternative to control bacteria in ethanol fermentations and able to efficiently replace antibiotics in ethanol production [12, 13, 86].

3. Concluding remarks and future trends

The idea of converting the brewing waste into functional ingredients is an area of research with huge potential and opportunities. Recent advances in biotechnology ensure that brewing industry by-products are no longer regarded as a waste but rather a feedstock for producing a new generation of added-value products. Based on this, it is an undeniable fact that brewing residues have their own potential for sustainable reuse through biotechnological processes. The recent findings highlighted the potential reuse of brewery by-product and led to the idea that multidisciplinary approaches should be implemented in order to develop integrated biorefineries. Despite the continuous progress in the recent years in this area, there are still the need and a priority to develop/adapt modern and efficient methods for extraction of these bioactive compounds.

As economic impact, using the BSG by-product, which has a low monetary value, as a high-nutrient biomass, will enhance the economic potential of breweries and improve the dietary attributes of food formulations. The recovered bioactive compounds and functional ingredients are also of great interest for food, pharmaceutical industry (e.g. antimicrobial activity, carrier agents, controlled release, immune-modulatory effects), cosmetics, agriculture, chemical industry and not only. The social impact of these actions refers to the fact that the complex recovery of bioactive compounds and new functional ingredients is aimed to be an efficient and at the same time affordable alternative, for all social categories, to complete their diet with an appreciable number of nutrients.

Taking into consideration all the above, the future trend in exploitation dewaste generated in the beer making process is represented by the development and optimisation of different integrated extraction system of biologically active compounds, thus maximising the valorisation efficiency of brewing waste, insufficiently exploited until now.

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