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Review of the Valorization Initiatives of Brewing and Distilling Byproducts

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Beer and spirits are two of the most consumed alcoholic beverages in the world, and their production generates enormous amounts of by-product materials. This ranges from spent grain, spent yeast, spent kieselguhr, trub, carbon dioxide, pot ale, and distilled gin spent botanicals. The present circular economy dynamics and increased awareness on resource use for enhanced sustainable production practices have driven changes and innovations in the management practices and utilisation of these by-products. These include food product development, functional food applications, biotechnological applications, and bioactive compounds extraction. As a result, the brewing and distilling sector of the food and drinks industry is beginning to see a shift from conventional uses of by-products such as animal feed to more innovative applications. This review paper therefore explored some of these valorization initiatives and the current state of the art.

Keywords: brewing; distilling; by-products; valorization; sustainability

1. Introduction

Brewing and distilling refer to the process of producing beer and spirits, respectively. Beer is a fermented alcoholic beverage made of malted/unmalted grains, water, yeast, and flavoured with hop. While spirit is a distilled alcoholic beverage made from grain derived alcohol. Beer and spirits are widely consumed across the world and hold significant shares in the world alcoholic beverage consumption. With a global production of 1.86 billion hL in 2021, beer is the most consumed alcoholic beverage while spirit is the third most consumed alcoholic beverage with global consumption of 35.26 billion litres in 2021 (Statista 2022). The implication of this is generation of equivalent amount of by-products materials (Figure 1) relative to the output of the sector. One of the most serious environmental issues faced by the brewing and distilling sector is by-products generation. This has led to research and studies in the space of brewing and distilling by-products which include proactive measures to enhance their

management and disposal. One of these measures is valorization, which is the repurposing of waste materials or by-products to convert them into a co-product with added value. There have been a lot of studies and initiatives in brewing and distilling by-products valorization, some of which are novel. The objective of this article was to review the current state of the art and novel valorization initiatives for brewing and distilling by-products (Table 1).

2. Spent Grain

Spent grain is the residue from used grains in brewing and distilling process, filtered from the wort after mashing protocol. In brewing, spent grain accounts for 85% of the total by-products with about 20 kg produced per hectolitre of beer (Bolwig et al. 2019). The annual production of wet brewer's spent grain stands at approximately 200 tonnes in Ireland, 8 million tonnes in Europe and 40 million tonnes worldwide (Mccarthy et al. 2013; Petit et al. 2020). Spent grain is a lignocellulosic biomass rich in proteins, lipids, minerals, and vitamins. Dried spent grain contains approximately 5 – 8% moisture, 1 – 5% ash, 14 – 30% crude protein, 3 – 10% lipids, 0.4 – 2.17% starch, and 50 – 70% total fibre (Table 2). These include about 16% cellulose, 28% hemicellulose, 7% lignin and various monosaccharides, oligosaccharides, and polysaccharides (Chetrariu and Dabija 2020; Mitri et al. 2022; Naibaho and Korzeniowska 2021). Predominant monosaccharides in spent grain include glucose, xylose, and arabinose while the predominant proteins include hordeins, glutelins, globulins, and albumins. Spent grain also contains micronutrients such as vitamins, minerals, amino acids, and polyphenols. The wet material can contain up to 80% moisture. Spent grain represents a major opportunity in the context of sustainable food transition being a large volume and nutrient dense by-product. One of the key factors in building a circular economy and creating sustainable production and consumption systems is the identification and

valorization of industrial by-products. The generation of large quantities of spent grain from brewing and distilling process have driven attention towards the development of different avenues for added value use beyond its traditional use in animal feed. At present, approximately, 70% of spent grain is utilised for animal feed (both wet and dry residue), 10% for biogas production, and 20% are disposed in landfills (Mitri et al. 2022). Its utilisation in animal feed is majorly attributed to its relatively high fibre and protein contents, and when combined with urea, it tends to provide all the essential amino acids required by ruminants, making it an excellent feed material (Chetrariu and Dabija 2020). In addition to its nutritional value for animals, spent grain has also been linked to increased milk production in cows (Chetrariu and Dabija 2020). However, the complexity of the chemical and nutrient profiles of spent grain has led to studies exploring its utilisation in other areas beyond its present predominant use as animal feed (Figure 2).

2.1 Valorization initiatives for spent grain

2.1.1 Spent grain in foods

The rich fibre, protein, vitamin, and mineral profile of spent grain make it a potential raw material for food product development and a high value material in the food market. Researchers believe it fits into the demands for healthy, protein-rich, plant-based foods. For its use in food, spent grain has been mostly converted into flour and used in a variety of bakery and pastry products. High protein flour from spent grain has been successfully incorporated into pastries and confectioneries. However, there are problems associated with the utilisation of spent grain in food which has been attributed to its complex nature and structure. Some of these problems include poor technological performance with respect to texture and other functional properties, off-flavour, off-

colour, and vulnerability to microbial spoilage. To take care of these problems, spent grain is being pre-treated by bioprocessing before its incorporation in foods. Bioprocessing involves the utilisation of live cells or cell components such as bacteria, chloroplasts to enzymes to achieve required foods attributes. For example, fermentation and enzymatic treatments have been employed to improve functional properties, nutritional quality, and overall acceptability of spent grain for both product development and fortification purposes. Bioprocessed spent grain has enhanced antioxidant activity, improved protein digestibility, and improved nutrient profile (Schettino et al. 2021). Verni et al. (2020) studied the effects of bioprocessed spent grain on its antioxidant potentials. In the study which utilised both enzymatic treatment and fermentation, the bioprocessed spent grain showed improved antioxidant properties characterised by high radical scavenging activity, long-term inhibition of linoleic acid oxidation, and protective effect towards oxidative stress. Bioprocessed spent grain can, therefore, be a novel ingredient in cereal-based or staple foods such as pasta, baked goods, and confectioneries. In another study by Schettino et al. (2021), bioprocessed spent grain was used to develop fortified semolina pasta, and this fitted into the label for "high fibre" and "high protein" according to EU Regulation No. 1924/2006. Spent grain has also been converted into a new protein-rich fibrous food stuff known as germinated barley flour (GBF), made by separating the husk fraction by milling and sieving (S. I. Mussatto, Dragone, and Roberto 2006). GBF contains the aleurone layer, scutellum, and germ fractions of barley malt. It is low in lignin and comprises mainly of non-cellulosic polysaccharides and glutamine rich protein (Kanauchi and Aoata 1997). GBF is considered prebiotic, anti-inflammatory, and functionally, it has high water holding capacity compared to other water insoluble dietary fibre sources. GBF is

reportedly safe and well tolerated in the body (S. I. Mussatto, Dragone, and Roberto 2006).

2.1.1.1. Source of phenolic compounds: The origin of spent grain makes it a good source of phenolic compounds. Phenolic compounds are chemical compounds synthesised naturally by plants, and they reportedly have bioactivities and antioxidant properties that can regulate inflammatory and oxidative stress as well as have prebiotic effects on gut microflora (Bertelli et al. 2021). Phenolic compounds are widely distributed in plants, and there is evidence to suggest that their ingestion have a negative correlation with physiological disorders such as cancers, diabetes, and cardiovascular diseases. Structurally, phenolics compounds have one or more aromatic rings with at least two hydroxyl groups. Two main groups of phenolic compounds are the non-flavonoids and flavonoids (Durazzo et al. 2019). The non-flavonoids include phenolic acids (hydroxycinnamic and hydroxybenzoic acids), xanthones, stilbens, lignans, and tannins. While the flavonoids include flavanones, flavonols, flavanols, anthocyanins, flavones, and isoflavones. Spent grain has been reported to be an abundant source of hydroxycinnamic acids (Chetrariu and Dabija 2020). Ferulic acid and p-coumaric acid are the most prevalent hydroxycinnamic acids in spent grain ranging from 0.35 to 4.90 mg/g dry matter and 0.067 to 1.80 mg/g dry matter, respectively (Chetrariu and Dabija 2020). Phenolic compounds in spent grain are recovered using different extraction techniques ranging from solid-liquid extraction, microwave and ultrasound assisted extraction, hydrothermal treatment, and enzymatic and alkaline reactions. They have been applied in foods mostly due to their antioxidant, antimutagenic, anti-inflammatory and antimicrobial properties (Sganzerla et al. 2021), and the main phenolic compound majorly extracted from spent grain is ferulic acid.

2.1.1.2 Source of dietary fibre: Spent grain have been reported as a good source of dietary fibre and these include polysaccharides, oligosaccharides, and lignins. Dietary fibres are classified according to their solubility in water, and these are soluble dietary fibres (pectins, gums, and mucilages) and insoluble dietary fibres (cellulose, hemicellulose, and lignin) (Dhingra et al. 2012). Dietary fibres have been recognised for their functional properties which has led to the development of fibre-rich products and ingredients within the food industry. These include water and fat holding capacities, swelling power, antioxidant capacity, and prebiotic activity (Rivas et al. 2021). Arabinoxylan, a type of dietary fibre from spent grain has been extensively explored and studied in spent grain valorization. In conventional arabinoxylan extraction, one tonne of spent grain can produce up to 133 kg arabinoxylan, a yield of 50% of untreated spent grain (López-Linares et al. 2020). The process involves alkaline pre-treatment, acidifying the alkaline extracts (pH 3) with citric acid, and the arabinoxylans recovered by ethanol precipitation (E. Vieira et al. 2014).

2.1.1.3 Source of protein: With increasing focus on plants protein extraction, spent grain have been utilised for this purpose. Usually, protein from spent grain is extracted simultaneously with arabinoxylan (Sganzerla et al. 2021). After ethanol precipitation to recover the arabinoxylans, the protein-rich fraction is then obtained using citric acid. This approach can recover up to 73% arabinoxylans and 85% proteins (E. Vieira et al. 2014). In the recovery of proteins from spent grain, hydrothermal pre-treatment at 60 ^{o}C has been proposed as it has the advantage of relatively lower cost, environmentally friendly, requires low temperatures, and does not need chemicals (Qin, Johansen, and Mussatto 2018). From an industrial perspective, protein extraction from spent grain can be done via enzyme-assisted fractionation process which involves hydrolysis of spent grain with alcalase enzyme (5 μL g−1) for 1 h (He et al. 2021). This can recover up to

46% protein and has a separation efficiency of 80%. According to a report by William G. Sganzerla et al. (2021), the scaled-up process for protein-rich fraction production requires a total capital investment of 11.2 million USD for an annual processing capacity of 590 tonnes of spent grain per day (He et al. 2021).

2.1.2 Spent grain as substrate

Synthesis of high value materials using microorganisms such as bacteria, fungi and yeast has been widely studied and explored. The nature and nutrient value of spent grain including its biological efficiency makes it a potentially good substrate material for this purpose. Hemicellulose in spent grain which ranges from 19 – 42% can be used in the synthesis of organic acids, amino acids, volatile fatty acids, enzymes, vitamins, and biofuels via fermentation (Dávila et al. 2016; Guarda et al. 2021; Mitri et al. 2022). Spent grain therefore meets the criteria and requirements of substrate material including cost and availability and has been as substrate material in these areas.

2.1.2.1 Bioethanol: Bioethanol is primarily produced from starch and sugar-based crops such as maize, sugarcane, rice, wheat, and sorghum (Oladeji and Alade 2016). However, these crops often conflict with food production as well as the consequences of land and materials use making its industrial production complex (Liguori et al. 2015). Waste lignocellulose biomass is now being exploited as an alternative material for bioethanol production. Spent grain is a lignocellulose biomass which is gaining worldwide interest as a low-cost abundant renewable resource material for bioethanol production. The hemicellulose and cellulose components of spent grain contain polymeric sugars, and these sugars can be liberated and fermented to produce bioethanol. Spent grain also contains grain husks and lignin which increases its value as a good feed material for ethanol production. Current practices for bioethanol production

using spent grain involve chemical or enzymatic hydrolysis to release fermentable sugars and then, microbial fermentation for alcohol synthesis. An alternative approach is the use of microorganisms in the hydrolysis stage. Some microorganisms can convert cellulose and hemicellulose in spent grain directly to ethanol through breakdown of the complex sugars, and subsequent fermentation of the resulting monomer units (Xiros et al. 2008; Xiros and Christakopoulos 2009). In general, production of bioethanol from spent can be divided into five steps – i. Spent grain pre-treatment (mostly with acid solutions), ii. Hydrolysis of the spent grain to breakdown the polysaccharides into simple fermentable sugars, iii. Fermentation of the sugars using microorganisms for ethanol production, iv. Distillation of the ethanol, and v. Drying of the ethanol to remove water (Solange I. Mussatto 2014). Up to 94 kg of ethanol can be produced from one tonne of spent grain using 36 hL of water according to the study by Wilkinson et al. (2017). Rojas-Chamorro et al. (2018) reported ethanol yield of 17.9 g per 100 g of spent grain with 69% of the total sugars converted to ethanol while Xiros et al. (2008) and Xiros and Christakopoulos (2009) reported yields of 74 and 109 g per kg of spent grain, respectively. In the study of one-pot bioethanol production from brewery spent grain using *E. coli*, Wagner et al. (2022) estimated a global yield of 251 L of ethanol per tonne of spent grain. Other studies that have successfully produced bioethanol from spent grain with promising yields are Liguori et al. (2015) and Pinheiro et al. (2019) both using enzymatic hydrolysis and *S. cerevisiae*.

2.1.2.2 Lactic acid: Lactic acid is a versatile chemical with a wide range of applications in food, pharmaceutical, cosmetic, textile and polymer industries. In food, it is used as an acidulant, flavouring agent and as a preservative. It is also used as a starting material for the manufacture of biodegradable poly-lactate polymers. Lactic acid is either produced by chemical synthesis or microbial fermentation of starch and sugar substrates

such as maize, potato, glucose, or sucrose (Abedi and Hashemi 2020). Nowadays, spent grain is being exploited as a medium for lactic acid production as a replacement for starch and sugars which are relatively costly and conflict with food production in their use for production of industrial feedstock. In the production of lactic acid from spent grain, the following 3 major steps are involved - i. Pre-treatment of the spent grain by either chemical or mechanical means to make the cellulose more accessible to enzymes, ii. Enzymatic saccharification to obtain a solution (hydrolysate) containing glucose as the main sugar, and iii. Fermentation of the hydrolysate by microorganisms, mostly *Lactobacillus spp.* (Pejin et al. 2017). Lactic acid from the hydrolysates of spent grain can have up to 91% yield according to the study by Pejin et al. (2017). Mussatto et al. (2007) and Assefa and Jabasingh (2020), also, successfully synthesised lactic acid from spent grain with different strains of *Lactobacillus* and obtained yields ranging from 50 to 70%. In current approaches, modern techniques to produce lactic acid allow the production of polylactic acid, which is a biodegradable plastic used in packaging, biomedical, transport, electronics, agriculture, and textile applications. To produce polylactic acid from spent grain, the glucose hydrolysate from spent grain undergoes fermentation by *Lactobacillus spp.* to obtain lactic acid. The obtained lactic acid is polymerised to produce the desired polylactic acid. The polymer is then purified and will be the precursor to produce bioplastics.

2.1.2.3 Xylitol: Xylitol is a natural food sweetener with similar properties to sucrose. It has found wide applications in the food and pharmaceutical industry because of its clinical properties. Industrial production of xylitol involves catalytic hydrogenation of D-xylose from hemicellulosic hydrolysates which is a high-cost operation requiring high temperature and pressure (Saha 2003). Alternatively, xylitol can be produced by microorganisms via fermentation. Xylose rich hemicellulosic materials including spent

grain, serve as abundant and cheap feedstocks for the synthesis of xylitol through fermentation (Solange I. Mussatto and Roberto 2005). To produce xylitol from spent grain, the feedstock is first hydrolysed with an acid to release the hydrolysate (xylose) which serves as the fermentation substrate. Dávila et al. (2016) developed a method for xylitol production from spent grain. In the study, xylose rich hydolysates (23 g/L) were concentrated to 70 g/L at 121 ^{o}C and 1 bar pressure and then fermented using *Candida guilliermondii* at 30 °C and 200 rpm. This yielded 0.78 g/g of xylose and 98.7% conversion rate of xylose. After fermentation, the CO_2 was separated, and the liquid stream filtered. The xylitol-containing liquid stream (0.58 g/L) was further concentrated at 40 ^{o}C and 1 bar of pressure followed by crystallisation of the concentrate.

2.1.2.4 Biobutanol: Butanol is an important liquid biofuel with energy value of 29 MJ/L very similar to gasoline which has energy value of 32 MJ/L (Plaza et al. 2017). Some of its other desirable properties as a biodiesel include being less corrosive, has low pressure, lower miscibility with water, and it can be transported in existing pipelines. Biobutanol is produced biologically from crops such as sorghum and non-feed feedstock such as grasses. An alternative to these is utilisation of agro waste and by-products, and spent grain falls into this category. The high cellulosic and hemicellulosic contents of spent grain makes it a great choice for biobutanol synthesis. Biological synthesis of biobutanol majorly involves fermentation using anaerobic *Clostridia* strains which produces acetone, butanol, and ethanol in the ratio 3:6:1, respectively (Luo et al. 2017). Plaza et al. (2017) studied the production of biobutanol from spent grain by first pre-treating the spent grain with sulfuric acid at pH 1 and 121 ^{o}C followed by enzymatic hydrolysis and fermentation by *Clostridium beijerinckii*. This yielded 75 g butanol/kg of spent grain and 95 g acetone-butanol-ethanol/kg BSG. In another study by Giacobbe et al. (2019), the spent grain was pre-treated with laccase to delignify and detoxify it

which helped to increase saccharification with no carbohydrates loss resulting in total hydrolysis of the polysaccharides fermentable sugars. These studies are an indication of the potential of biobutanol production from spent grain.

2.1.2.5 Energy and Biogas: Spent grain has been proposed for use in energy production either through direct combustion or through fermentation to produce biogas. Biogas is a mixture of 60 to 70% methane, carbon dioxide and small proportions of hydrogen, nitrogen, and carbon monoxide (S. I. Mussatto, Dragone, and Roberto 2006). It is produced by digestion of organic residue in an oxygen free environment, otherwise known as anaerobic digestion (Ghasemi et al. 2018). Biogas production from spent grain involves two stages. First, is the hydrolytic stage which allows for the total breakdown of the spent grain, a crucial step towards obtaining high yields of biogas. The second stage is the methanogenic stage where acidogenic microorganisms convert complex macromolecules of the spent grain into volatile fatty acids, acetates, butyrate, and propionate, followed by a subsequent conversion of these volatile acids by methanogenic bacteria into methane gas (Solange I. Mussatto 2014). Combustion and biogas energy production from spent grain has been evaluated for reuse in brewing and it was concluded that the technology is well suited for the generation of thermal energy in breweries (Zanker and Kepplinger 2002). The gas produced is pure, CO_2-free, and may be utilised in fuel cells to create energy. However, even though biogas is recyclable, efficient, and clean, it is made with fossil combustibles which has raised environmental concerns regarding its production.

2.1.3 Adsorbent

With increasing diversity of raw materials for biosorbents, natural organic raw materials are now being exploited for green adsorbent production. These ranges from hazelnut

shells to chitosan, nanocellulose, starch and saw dust (Su et al. 2021). These biosorbents have advantages of being low cost, easy to functionalise, possibility of further volume reduction by pyrolysis (thermal decomposition in the absence of oxygen) and being biocompatible and non-toxic for animal and human health applications (Su et al. 2021). Spent grain is one of the natural organic raw materials that been exploited as a biosorbent. Its relatively low cost and abundant surface functional groups makes it a viable adsorbent material in applications such as biochar production and adsorbent material for organic dyes, heavy metals, waste gases and volatile organic compounds. Vanreppelen et al. (2014) studied production and adsorption properties of activated carbon from spent grain pyrolysis. The different activated carbons produced had yields of 16 – 24% by weight, with adsorption properties comparable to that of commercial activated carbon used as a control for the experiment. For water treatment, Su et al. (2021) studied the feasibility of spent grain utilisation as a biosorbent for uranyl ion removal from wastewater. Results from the study showed that spent grain as a biosorbent favoured oxidation and yield of high carboxyl group content of the biosorbent. It exhibited high adsorption capacity and fast adsorption kinetics of one hour which compared well with other biosorbents reported in literature (Su et al. 2021). In dye adsorption studies, Chanzu et al. (2019) demonstrated that spent grain was a viable cost-effective sorbent material for wastewater decolourisation. Utilisation of pyrolyzed spent grain as an adsorbent to remove volatile organic compounds from waste gases reportedly had adsorption capacity like that of coconut shell charcoal (Guido and Moreira 2017). Activated carbon from spent grain for water and gas purification is gotten by alkaline treatment to recover lignin. This is followed by sulphuric acid precipitation and phosphoric acid activation of the recovered lignin at 600 ^{o}C (Solange I. Mussatto 2014).

2.1.4 Brick and paper production

A process to produce brick and paper from spent grain has been trialled and developed. As a brick component, the low ash content of spent grain and its high fibrous material makes it suitable for use in building materials. When spent grain was incorporated into bricks, it improved the dry characteristics of the bricks without compromising the colour and quality. The production process required no alterations, making it a suitable substitute for sawdust in brick making (Russ, Mörtel, and Meyer-Pittroff 2005). In the study by Russ et al. (2005), bricks produced with spent grain had higher strength, higher porosity, and reduced density after firing than the ones made from standard clay production. In the production of red brick ceramic paste, incorporation of spent grain promoted the brick's porosity and water holding capacity, and reduced density and thermal conductivity, which are all desirable attributes in brick making. This means that spent grain can be used to enhance the rigidity and insulating properties of brick (Ferraz et al. 2013). Also, the fibrous nature of spent grain has led to its investigation for use in paper production and utilisation in the production of high-grade texture paper towels, business cards, and coasters (IshiwakiI et al. 2000). However, paper made from spent grain had poor structural strength properties but has the potential for use as a corrugating medium.

2.1.5 Sustainable packaging

Spent grain has potential as a raw material for the development of sustainable packaging within the food industry. The development of biodegradable sustainable packaging from spent grain was attributed to the ability of the proteins in spent grain to interact with the polypeptide chains (Chetrariu and Dabija 2020). In addition, cellulose which is a major component of spent grain has been utilised in food packaging because of its fine

network, biodegradability, and strong water resistance. Cellulose from spent grain can therefore be exploited for this purpose. Spent grain is now being transformed into a paperboard alternative to be utilised for six-pack beer carriers (InGrain 2016). Formela et al. (2017) studied different polyurethane (a class of fibrous compounds) rations from spent grain. The study showed that the polyurethane from spent grain had improved physical property and mechanical properties with enhanced thermal stability. The apparent density and compression resistance increased by 37% and 50%, respectively (Formela et al. 2017). For its use in packaging, plasticisers are added to help reduce fragility of the film and enhance plastic properties such as flexibility and film handling. Chitosan incorporation in spent grain can result in microfilms with antibacterial and antioxidant qualities (Nazzaro et al. 2018). Protein-protein interactions, which are pH dependent, have the greatest effect on film formation. Obtained films can be used as a UV barrier because they no transmission between 200 and 400 nm (Proaño et al. 2020), and this together with the antimicrobial and antioxidant properties of the film can be exploited for use in active packaging (Chetrariu and Dabija 2020). Films containing spent grain arabinoxylan have enhanced thermal and mechanical properties in addition to antioxidant properties of the arabinoxylan extract. This packaging initiative can be employed in active food packaging and may serve as an alternative to traditional and synthetic food additives in packaging technology. Spent grain also has potential use as natural binders in compression moulded products and can replace polystyrene in food packaging materials.

3. Spent Yeast

Spent yeast is the by-product of wort fermentation in breweries. It is the second most relevant by-product of the brewing process, and accounts for up to 15% of total by-products from brewing operations (Rachwał et al. 2020). Approximately 1-3 kg of

surplus yeast (wet basis) is generated for every hectolitre of beer produced (Jacob et al. 2019). In brewing, yeast is pitched into the fresh wort to initiate the fermentation process. Spent yeast results after the pitched yeast has exhausted its fermentative purposes by a process known as flocculation. The most common disposal and management practice for spent yeast is its use by farmers in animal feed or in some cases as compost. Spent yeast being a nutrient dense by-product containing a lot of bioactive compounds has the potential of becoming a more valuable by-product beyond this prominent end use. Spent yeast has a high moisture content ranging from 74 – 86%, dry matter content of about 10 – 16%, and ash content of 2 – 8.5% (Rachwał et al. 2020). It is a chemical rich by-product comprising of majorly proteins and carbohydrates. The residue has been reported to contain about 40% crude protein, 59% total carbohydrates (of which 23% are β-glucans) and 1% lipids (Thammakiti et al. 2004). The predominant amino acids in spent yeast according to Fărcaş et al. (2017) are leucine, lysine, tyrosine, arginine, cysteine, histidine, isoleucine, methionine, phenylalanine, threonine, tryptophan, and valine. This makes it a good source of high-quality protein material and its high β-glucan content makes it a good source of dietary fibre. Spent yeast also contains several phenolic and bioactive compounds most of which have been absorbed from the grain or malt during fermentation. Some of the known phenolic compounds contained in spent yeast include gallic acid, protocatechuic acid, catechin, and the hydroxycinnamic acids – p-coumaric and ferulic acids (Podpora et al. 2015; Rizzo et al. 2006). Despite the rich nutrient profile of spent yeast, its use in human nutrition is limited. This is because of its high level of nucleic acids (6 – 15%) which can increase uric acid levels in the blood and tissues causing hyperuricemia or the deposition of uric acid in joint tissue (Jaeger et al. 2020). Nonetheless, there are a lot of potential and novel uses for spent yeast both in the food industry and beyond such as

functional food applications, substrate for bio-reactions and agents for biosorption processes.

3.1 Valorization initiatives for spent yeast

3.1.1 Functional food applications

A novel approach in the added value use for spent yeast is in the development of functional foods. Spent yeasts is known to contain several bioactive components ranging from β-glucan, saccharides, and extracts. Advances in food science research supports the hypothesis that foods in addition to their nutritional roles can also have added health benefits, hence, the interest in functional foods. To drive innovation in functional foods production, a new generation of functional foods is focused on exploiting unconventional sources of bioactive compounds for new food products creation. Spent yeast has found novel uses in this area as one of the novel unconventional sources of bioactive compounds in different applications. β-glucan from spent yeast reportedly has a multi-directional biological activity because of its unique combination of β-(1→4) and β-(1→3) linkages of long chain polysaccharides having high molecular weight (Jaeger et al. 2020; Rachwał et al. 2020). The high molecular weight of β-glucan generates high viscosity in the gut which has been reported to be the reason behind its health benefits (Henrion et al. 2019). Some of these health benefits include ability to improve the immunology of humans/animals, prebiotic and antioxidant effects, ability to improve blood lipid content, increasing satiety, and reduction of postprandial glucose response (Henrion et al. 2019; Rakowska et al. 2017). β-glucan is a high value ingredient for functional food development, and spent yeast is proving to be a good source for its extraction. β-glucan levels can increase in yeast cells during fermentation because of changes in the cells that allow for optimal use of sugars

in the wort (X. E. Li et al. 2018). In addition to the β-glucan content of spent yeast, it is also a good source of antioxidants. The antioxidant properties of spent yeast mainly come from polyphenols absorbed by the yeast from external sources (such as malt and hop) during fermentation. Spent yeast contain high levels of gallic acid, protocatechuic acid, catechin, p-coumaric, ferulic and cinnamic acids both in the free and bound forms (Podpora et al. 2015), and this has been found to even increase further during enzymolysis (E. F. Vieira, Melo, and Ferreira 2017). In a study by Marson et al. (2019) on the influence of sequential enzymolysis on antioxidant properties of spent yeast, it was reported that internal cell components were more liberated resulting in a 63% increase in antioxidant qualities. This is an indication that spent yeast has the potential to become a high value industrial source of polyphenols.

3.1.2 Techno-functionality in foods

3.1.2.1 Emulsifying, stabilising, binding, and thickening agent: Spent yeast presents a sustainable and technological viable option for use as emulsifying, stabilising, binding, or thickening agent. β-glucan and mannoproteins found in spent yeast possess emulsifying, stabilising, binding, and thickening properties. They have been applied in foods for these purposes. The potential of spent yeast as a source for improving functionality in food was studied by extraction of the β-glucan using autolysis (Thammakiti et al. 2004). The extracted β-glucan from spent yeast was tested alongside commercially available products, and it was found to have higher apparent viscosity, water holding capacity and emulsifying property more than the commercial products. The potential of β-glucan and mannoproteins from spent brewer's yeast as either an emulsifying, stabilising, binding, or thickening agent in food products has been studied in baked foods (Martins, Pinho, and Ferreira 2018), mayonnaise (Silva Araújo et al. 2014), and ham (Pancrazio et al. 2016). When compared to standard flour, β-glucan rich

flour (2 g β-glucan per 100 g flour) generated loaves with larger specific volume and more consistent pore structure, which was attributed to the stabilizing impact of -glucan on gas cells in the loaf (Jaeger et al. 2020).

3.1.2.2 Flavouring agent: Yeast extract from spent yeast has the potential of serving as a natural biological flavouring agent. Spent yeast contains up to 10% nucleic acids (Jaeger et al. 2020) including peptides and amino acids which makes it a good source of the 5'-nucleotides which has been used at an industrial scale for taste and aroma development in soups, bouillons, and gravies (Rachwał et al. 2020). During autolysis, the intracellular enzyme nuclease in the yeast produces nucleotides and nucleosides namely, 5'-guanosine monophosphate and 5'-inosine monophosphate (Fărcaş et al. 2017). 5'-guanosine monophosphate and 5'-inosine monophosphate are both flavour enhancers of which the latter's flavour-enhancing power is 100 times more than that of monosodium glutamate (E. Vieira, Brandão, and Ferreira 2013). In addition, the yeasts breakdown the proteins into smaller polypeptides and sulphur amino acids which acts to improve tastiness, mouthfulness, and flavour development (Fărcaş et al. 2017). The flavour enhancing property of yeast extract from spent yeast is attributed to the synergy of the different compounds of peptides, nucleotides, amino acids, and carbohydrates (Rakowska et al. 2017). Naturally, these are intensified during fermentation as yeasts can synthesise a myriad of flavour molecules (Marson, de Castro, et al. 2020). Yeast extract from spent yeast can be applied in a variety of foods as flavour enhancers and can potentially replace glutamates and hydrolysates (Ferreira et al. 2010; E. Vieira, Brandão, and Ferreira 2013). It is important to note that the potential use of yeast extract from spent yeast as a flavouring agent depends to a large extent on the method used for its disruption and processing (Marson, de Castro, et al. 2020). The method used will determine the level of concentration of amino acids in the extract as well as the

interactions between the amino acids, nucleotides, carbohydrates, and peptides present in the extract. Manipulation of the yeast extract preparation methods can be used to develop a wide range of different flavours. Meat flavours in the extracts have been developed by reaction between 5'-nucleotide glutamic acid and cysteine which can be intensified by thermal treatment (Rakowska et al. 2017). Thermal treatment can hasten cell disintegration and the formation of new flavour compounds (Jaeger et al. 2020), and this has been studied by (Alim et al. 2019). Jacob et al. (2019a) compared the amino acid composition of yeast extracts prepared by mechanical disruption and autolysis and found that autolysis gave a better yield of the amino acids. Amino acid concentration in the extract plays a vital role in its flavouring potency. Spent yeast is classified as GRAS which means that there are no safety concerns with respect to its use as a flavouring agent (Jung et al. 2010). This means that it can become an important source for some of these flavour compounds if properly harnessed.

3.1.2.3 Encapsulating agent: Yeast materials have been evaluated as an encapsulating agent because of their wide range of desirable functional properties such as gel formation, stabilisation, and emulsification properties. Marson et al. (2020b) studied the possibility of spent yeast as an ascorbic acid encapsulating agent, a common but very unstable dietary component. In the study, spent yeast based Maillard reaction products were used to encapsulate ascorbic acid by spray drying. Reported results showed that spent yeast based Maillard reaction products resulted in particles of high encapsulation yield of 102%, and a well retained shape and structure when viewed under scanning electron microscope. The presence of yeast cell debris on the surface of the particles was confirmed by Fourier transform infrared spectroscopy (FT-IR) which served as evidence of effective encapsulation. Paramera et al. (2023) and Shi et al. (2010) reported that cells of *Saccharomyces cerevisiae* after chemical treatment exhibited high

encapsulation yields for chlorogenic acid (a natural hydrophilic antioxidant). In the production of aerogels for drug administration, yeast β-glucans performed better than barley β-glucans with respect to stability, elasticity, resistance to compression stress, and water absorption capacity (Salgado et al. 2018). In another similar study by da Silva Guedes et al. (2019), yeast β-glucans (extracted from brewery slurry) were compared with fructooligasaccharides for their preservative abilities in the lyophilisation and storage of probiotic lactobacilli to keep the cells viable and active. The study showed that the cryoprotectant effects of spent yeast β-glucan were like that of fructooligasaccharides which is a known cryoprotectant (Jaeger et al. 2020).

3.1.3 Enzyme source

Yeasts contain different enzymes with hydrolytic activity, and it is a source for extraction of these enzymes for use in different applications. Enzymatic extracts of spent yeast are being employed alone or in combination with other exogenous enzymes to synthesise protein hydrolysates (Q. Li et al. 2022; E. F. Vieira, Melo, and Ferreira 2017). To minimize enzyme denaturation and loss of hydrolytic ability, protein extract from spent yeast is often prepared by autolysis of yeast cells under refrigeration (Marson, Saturno, et al. 2020). There have been studies on the utilisation of spent yeast proteases for the synthesis of sardine protein hydrolysates. Results showed that the hydrolysates had antioxidant and ACE inhibitory properties with increased emulsion, foaming and oil-binding properties (E. F. Vieira, Pinho, and Ferreira 2017). Spent yeast is also high in invertase and pectinases. This is because *Saccharomyces cerevisiae* is a known source of invertase, and this has been extracted from spent yeast using autolysis and ultrafiltration. Crude pectinases extracted from spent yeast were effective in boosting the yields of pineapple and pawpaw juices (Dzogbefia et al. 2007; Pérez-Torrado et al. 2015). Spent yeast also showed ability as a good medium for lactic acid

bacteria producing proteolytic enzymes. Mathias et al. (2017) demonstrated this potential in their study with a final proteolytic extract of 145.5 U/g.

3.1.4 Substrate for microbial growth

The nutrient profile of spent yeast makes it a potential substrate for microbial growth or product formation involving microbial synthesis. Its low carbon to nitrogen ratio makes it even more desirable as an additive for fermentation media in the synthesis of high value compounds utilised in the food industry (dos Santos et al. 2015). Champagne et al. (2003) studied the effect of spent brewer's yeast extract on the growth of *Lactobacilli* and *Pediococci* and Mathias et al. (2017) evaluated brewer's spent yeast potential as a growth media for lactic acid bacteria. For utilisation as a substrate, mainly, hydrolysates and autolysates which are both gotten from spent yeast are used (Ferreira et al. 2010). Microorganisms growing on spent yeast release extracellular proteolytic enzymes which reportedly have the highest potential as an additive for protease synthesis (Rachwał et al. 2020). Autolysates from spent yeast were utilised in the production of ethanol by recombinant *Escherichia coli* and in the production of *Lactobacillus acidophilus* in beetroot and carrot juices while spent yeast hydrolysate was used as a nitrogen source in succinic acid production by *Actinobacillus succinogenes* (York and Ingram 1996). The chemical profile of spent yeast showed that it has the potential of being used as a supplement for fermentation media and for the growth of specific microorganisms used in functional foods.

3.1.5 Yeast extract

Spent yeast is a rich and cost-effective feed material for yeast extract production. Yeast extract is the part of the yeast cell wall that is still soluble after the cell wall has been damaged and removed is known as yeast extract (Jaeger et al. 2020). The distribution of

physiologically relevant components in yeast extract is influenced by its composition. Yeast extract is a common food additive utilised as a flavour agent and nutritional additive in broths, soups, and condiments due to its unique characteristic umami flavour and meaty aroma (Dimopoulos et al. 2018). It is also used as a protein enhancer in food manufacturing and ingredients formulation due to its high protein content, good amino acid balance, and high concentration of B-vitamins (Pérez-Torrado et al. 2015). To obtain yeast components suitable for use in food manufacturing and nutraceutical applications, spent yeast can be transformed into yeast extract production using its autolysate or hydrolysate (Figure 3). This process is temperature, pH, and time dependent and requires the addition of autolysis enhancing agents. The soluble part is the yeast extract, and it is equivalent to the protein concentrate released naturally by the cell after degradation of the intracellular component (Pozo-Bayón et al. 2009). The method chosen for the cell wall disruption for yeast extract production can have effect on the composition and characteristics of the yeast extract, and this can be manipulated to obtained different flavour profiles and quality traits (Rakowska et al. 2017). The method for yeast extract production can be either by autolysis, hydrolysis, or plasmolysis. The addition of acids or proteolytic enzymes is known as hydrolysis, and the self-digestion of the cell by its own enzymes is known as autolysis. In autolysis the cellular components including proteins, glycogen and nucleic acids are solubilised by the activation of degradative enzymes contained in the cells (Šuklje et al. 2016). Autolysis of the yeast cell occurs during the beginning of the cell's death phase, producing partial disintegration of the cell wall and allowing for the extraction of important components without causing damage to their original structure (Podpora et al. 2015). Plasmolysis is modified autolysis process where “accelerators” such as organic solvents and inorganic salts are added to aid cell breakdown (Jaeger et al. 2020).

Several strategies for disrupting yeast cell walls and their impact on yeast extract composition have been investigated. The downsides of autolysis include small extract yield, difficult phase separation because of the significant quantity of residue in the hydrolysate, high possibility of microbiological contamination, and relatively poor organoleptic properties (Bayarjargal et al. 2011). Yeast extract produced from spent yeast using ultrasonic sonotrode had elevated amounts of protein, fat, trehalose, B-vitamins and biologically active 5-methyltetrahydrofolate (Jacob et al. 2019). Combinations of autolysis, enzymatic hydrolysis, and selective membrane filtering have also been studied as innovative processing strategies yeast extract production (Jaeger et al. 2020). To obtain its full potential, spent yeast must be efficiently isolated from the bulk before being processed into yeast extract. Spent yeast has a distinct bitter flavour, which is mostly due to hops employed in the brewing process, as well as tannins and resins that adhere to the yeast cell walls during fermentation (Shotipruk et al. 2005). This might be a problem when producing yeast extract from spent yeast. To avoid this, spent yeast can be pre-treated with alkaline or organic solvents before processing (Jaeger et al. 2020). Shotipruk et al. (2005) proposed that the debittering stage be performed concurrently with the cell debris separation.

3.1.5.1 Yeast cell wall: Yeast cell wall is the insoluble component of the autolysate produced during yeast extract production. Its components include mannans, β-glucans and glycoproteins which are all carbohydrates found in yeast. β-glucans are the building blocks of yeast cell wall, and they have wide applications in food (Thammakiti et al. 2004), and they can be made from yeast cell wall that has been recovered during spent yeast autolysis. To achieve this, the cell wall is homogenised with an alkali to extract the β-glucans. Then the extract is washed with acid and water, respectively. The resulting β-glucan is a light-tan coloured paste with acidic pH of about 4.3 and

approximate composition (w/w) of 93.37% moisture, 0.07% fat, 0.04% ash, 0.38% protein, and 6.13% carbohydrate (Worrasinchai et al. 2006).

3.1.5.2 Ribonucleotides: Ribonucleotides can be extracted from yeast biomass using either hydrolysis, plasmolysis, or autolysis. However, autolysis is the most used ribonucleotides extraction method from yeast biomass (Jae-Ho, Byung-Hoon, and Jong-Soo 2002). During this process, endogenous enzymes found in yeast break down RNA, releasing 2 '-, 3'- or 5'- ribonucleotides from the microorganism (Alves, de Souza, and de Oliva Neto 2021). Ribonucleotides with 2'- and 3'-phosphate groups are of little economic importance, but the 5'-ribonucleotides are high value compounds which are widely utilised in the food and pharmaceutical industries because of their bioactive properties (Alves, de Souza, and de Oliva Neto 2021). Chemical hydrolysis is known to extract all ribonucleotides RNA components but with little specificity, whereas enzymatic treatment will produce specific ribonucleotides making it the main ribonucleotides production method (Jae-Ho, Byung-Hoon, and Jong-Soo 2002). Enzymatic hydrolysis according to Deoda and Singhal (Deoda and Singhal 2003), is less difficult, more inexpensive, and produces greater yields of ribonucleotides than other methods of 5'-ribonucleotide production. According to Grand View Research, Inc (2019), the global demand for nucleotides at about 800 million dollars (Alves, de Souza, and de Oliva Neto 2021). This market prognosis for nucleotides implies that nucleotide extraction from spent yeast biomass may be used to capitalise on this market advantage. 5'-ribonucleotides rich yeast extracts, particularly 5'-inosine monophosphate (5'-IMP), 5'-guanosine monophosphate (5'-GMP), and monosodium glutamate (GMS), are known to improve flavours and induce softness in soups and sauces (Löliger 2000).

4. Trub

In brewing, trub refers to the sediment left in the whirlpool or hop-back after the wort has been boiled and transferred for cooling. It results from precipitation of high molecular weight compounds during wort boiling (Lomuscio et al. 2022). After boiling, the wort is transferred into the whirlpool where the trub is separated. About 0.2 – 1.4 kg of trub (wet basis) is generated for each hectolitre of beer produced, and this ranges from 0.21 – 0.28 $kghL^{-1}$ for hop pellets and 0.7 – 1.4 $kghL^{-1}$ for whole hop cones (Evans 2006). Trub mostly contains insoluble denatured proteins, complex carbohydrates, lipids, tannins, and other mineral compounds (Kühbeck et al. 2018). The proportion of the individual components in trub will vary depending on the raw materials used in the brewing process. Approximately, it contains about 40 – 70% protein, 7 – 32% bitter components, 20 – 30% phenolics, 4 – 8% carbohydrates, 1 – 8% fat, 5% ash and 1 – 2% bitter acids (Sterczy´nska et al. 2021). Trub has particle sizes varying from 30 – 140 µm and can reach up 500 µm in some cases depending on the type of hop used (pellets or whole cones) (Stachnik et al. 2021). The suitability of trub for animal feed is limited by its bitterness contributed in part by the hops. Trub has been trialled for pig feed in combination with dried protein feed preparations to reduce the bitterness and make it more acceptable for the animals (Rachwał et al. 2020). Saraiva et al. (2019) developed an extraction method for reducing the bitterness in trub while still maintaining its quality profile which will help increase its value for utilisation in foods. Trub has been proposed for the enrichment of fat-rich foods and as an alternative source of vegetable protein (Saraiva et al. 2019). Lomuscio et al. (2022) fortified durum wheat fresh pasta with debittered trub and up to 10% trub addition did not compromise the quality and sensory characteristics of the final product. Trub is known to have antimicrobial properties which is contributed by spent hops in the trub. This property allows for the possibility of utilising trub as fertilizer or pesticide (Kerby and Vriesekoop 2017;

Sterczy´nska et al. 2021). Trub has a high concentration of sesquiterpenes and can be utilised to make natural and low-cost insect repellents for food storage (Kopeć et al. 2021). Tesio et al. (2020) studied the preparation of non-activated porous carbon from trub for high performance lithium-sulphur batteries. The trub was employed as an effective cathode in lithium-sulphur batteries after a high sulphur loading of up to 70%. The resultant cathode performed excellently, with high-capacity values and long-term cyclability at high current. Another possible valorization option for trub is as an additive in fermentation media for bioprocesses due to its carbon-nitrogen ration. The carbon-nitrogen ratio of trub resembles that of microbial cell composition which exerts positive effect on cell division, hence, it can be effectively used as a supplement in cell cultures (Rachwał et al. 2020).

5. Spent Kieselguhr

Kieselguhr also known as diatomaceous earth or just diamomite is a non-metallic, soft, brittle, fine-grained, and siliceous sedimentary rock that may be readily broken into a white to off-white powder (Ferraz et al. 2011). The high porosity of the powder imparts physical properties of lightness and granular feel to kieselguhr. Due to its unique porous structures, high adsorption capacity and low density, kieselguhr is widely used in brewing as a filter aid for beer filtration process (Russ et al. 2006). Spent kieselguhr in brewing is the waste generated from the kieselguhr which has been used in beer filtration. Approximately, 3.78 million tonnes of spent kieselguhr is generated from breweries annually across the globe (Nanayakkara, Gunathilake, and Dassanayake 2022). In the filtration of beer during brewing, one litre of beer uses approximately 1 – 2 g of kieselguhr which generates about 17.14 g of spent kieselguhr per litre of beer on a wet basis (Gong et al. 2019). Reportedly, the conventional disposal route for spent kieselguhr is landfilling, composting or application in organic fertilizer which have

disadvantages of wasting land resources, environmental pollution, and risk of leaching nitrogenous substances into the ground (Gong et al. 2019). One of the proposed routes for sustainable management of spent kieselguhr waste is its regeneration as an adsorbent material. Kieselguhr is highly porous, has a wide surface area with low thermal conductivity and high amount of active silanol groups (Si−OH) on the surface (Gong et al. 2019). The ionisation of the silanol groups can cause a negative charge to form on the diatomite surface, a property which can remove organic contaminants and heavy metal cations from wastewater (Zhao et al. 2019). Kieselguhr has been studied as a possible adsorbent for removing dyes and heavy metals from textile and tanning effluents (Al-Ghouti et al. 2009; Al-Qodah et al. 2007; Gürü, Venedik, and Murathan 2008), and there is potential for reuse of brewery spent kieselguhr as an adsorbent after biological regeneration. In the study by Gong et al. (2019), laboratory regeneration of spent kieselguhr using ammonifying bacteria after a 14-day incubation significantly degraded accumulated proteins and enhanced the surface performance and pore structure of the spent kieselguhr. When used in adsorption studies, the bio-regenerated spent kieselguhr were able to remove up to 95.5% of methylene blue dye and 71.7% of chromium ion (Gong et al. 2019). In another similar study by Huaccallo Aguilar et al. (2022), geopolymers from spent kieselguhr were utilised in the treatment of winery wastewater and when used as adsorbents were efficient in the removal of high concentrations of organic pollutants from the wastewater material. Another proposed route for sustainable utilisation of spent kieselguhr is its use in construction for brick production (Mateo et al. 2016; Nanayakkara, Gunathilake, and Dassanayake 2022). When clay was mixed with spent kieselguhr, it decreased fuel consumption during firing by reducing vitrification temperature and adding additional calorific value from organic matter in spent kieselguhr (Eliche-Quesada et al. 2011). The porous nature of

spent kieselguhr increases porosity of bricks and can be exploited for the manufacture of lightweight calcium silicate brick with good thermal insulating properties (Pimraksa and Chindaprasirt 2009), and reduction of bulk density especially in ceramic bricks (Nanayakkara, Gunathilake, and Dassanayake 2022). Ferraz et al. (2011) studied the production of ceramic bricks from recovered brewing spent kieselguhr. The study showed that no significant loss nor constraint was found in both the mechanical properties and ecotoxicity value of ceramic bricks made from brewing spent kieselguhr (Ferraz et al. 2011). Some of the characteristics that make spent kieselguhr a good co-product for brick production include its silica-rich particles, high porosity, lightweight, and thermal insulation (Nanayakkara, Gunathilake, and Dassanayake 2022). Despite these attributes, spent kieselguhr is yet to be incorporated in commercial brick production, and the need for the development of standards.

6. CO_2

CO_2 produced during wort fermentation in brewing and distilling is a valuable by-product that can be recovered for reuse either within the facility or sold for other purposes. This makes for best environmental management practice in brewing and distilling especially in sustainable production for a greener process with low emissions and reduced carbon footprint. CO_2 when recovered is scrubbed, purified, and compressed for reuse within the facility or storage for other purposes (Figure 4). CO_2 recovery can be adapted for all scales of breweries and distilleries; however, microbreweries and small-scale distilleries might be less inclined in setting up a CO_2 recovery process due to the expense and complexity of the system (European Commission 2015). For a CO_2 recovery system, its environmental performance indicators are amount of CO_2 recovered from the fermentation process, amount of CO_2 recovered per unit of output and the capacity of the CO_2 recovery system (European

Commission 2015). For an effective system, the benchmark is minimum recovery of least 50% of CO_2 produced during wort fermentation (European Commission 2015). The need to scrub and purify recovered CO_2 from wort fermentation is because it contains impurities such as hydrogen sulphide, oxygen, and dimethyl sulphide (Buchhauser et al. 2008). These compounds have negative effects on taste, odour, and shelf life of products. In beer fermentation, about 4 kg of CO_2 is produced per hectolitre of beer, and of these, at least 2 kg can be successfully recovered using currently available developed CO_2 recovery systems (Lawrence et al. 2003). This is sufficient to meet the carbonation needs of breweries as a typical brewery requires an estimated 2 kg of CO_2 per hectolitre of beer (Manger 2010). CO_2 recovery is of interest especially to brewers as CO_2 is required for purging and carbonation. Oxygen in final product reduces product shelf life as well as its organoleptic qualities, and it is difficult to separate the initial high concentrations of N_2 and O_2 in the CO_2. To minimise this, CO_2 recovery must start 24 hours after the start of fermentation to ensure that the incoming fermentation gas has a minimum CO_2 concentration of 99.5 % (European Commission 2015).

7. Pot ale

Pot ale is the liquid by-product of whiskey distillation. It is the liquid residue left in the wash still after the first distillation process. Large quantity of pot ale is produced in distilleries during the distillation process, making it the most significant by-product of whiskey distillation. Physically, pot ale has a caramel colour and is highly turbid. It contains about 5% solids, residual barley and yeast from the wash, soluble proteins, carbohydrate, and variable levels of copper (White et al. 2020). It is reported that an average of 8 litres of pot ale is generated for every litre of pure alcohol produced (Mohana, Acharya, and Madamwar 2009). The most common adopted end use for pot

ale is its use as animal feed. It is mostly fed to pigs, can be mixed with spent grain to produce distillers' dark grain (also used as animal feed) or concentrated by evaporation to get the pot ale syrup which is a nutrient-rich ruminant feed (White et al. 2020).

7.1 Valorization initiatives for pot ale

7.1.1 Recovery of lactic acid

Lactic acid, a high value industrial chemical and a major constituent of polylactic acid can be recovered from pot ale. Significant concentration of lactic acid has been found in pot ale with average concentration of 120 mg/L (Graham et al. 2012). This was linked to the occurrence of lactic acid bacteria during mashing and fermentation, which produce lactic acid. Recovery of lactic acid from pot ale would have the advantage of being a completely downstream process, resulting in much lower operational costs than traditional fermentative production. An estimated 2.2 kilo tonnes of lactic acid per year have been projected as the potential lactic acid that can be recovered from pot ale across major whiskey producing countries of the world (Table 3). This is more than the present market demand for lactic acid (McNerney 2019).

7.1.2 Recovery of phosphate

Phosphate is widely used in agro-allied industries for the production inorganic fertilizer, and because mined phosphate is a limited resource, recovering phosphate from waste streams such as pot ale is desirable. Phosphate concentrations in pot ale can reach up to 0.5 g/L (Dionisi, Bruce, and Barraclough 2014). Precipitation and absorption are some of the different methods that can be used to recover phosphate from pot ale. There has also been research into the possibility of pyrolyzing anaerobically digested sewage sludge to make biochar (Shepherd, Sohi, and Heal 2016). Biochar has a strong affinity

for aqueous phosphorus, and this can be exploited for the recovery of phosphate from pot ale (Shepherd, Sohi, and Heal 2016).

7.1.3 Anaerobic digestion

The chemical oxygen demand (COD) is considerably high, it is easily biodegradable making it a suitable base material for anaerobic digestion. The biogas produced by the anaerobic digestion of pot ale can be used to generate heat and power for various purposes. However, there are limitations to the use of pot ale in anaerobic digestion. First, the yeast components that contributes significantly to the chemical oxygen demand of pot ale can accumulate at the base of the reactor, creating problems with digestion stability (Goodwin, Finlayson, and Low 2001). Second, the protein in pot ale can cause ammonia to build up in the reactor, which inhibits methanogenesis (Mahdy et al. 2017).

8. Spent botanicals

Spent botanicals is a by-product of gin distillation. Gin contains juniper as the base botanical with other botanicals ranging from coriander, angelica, orris root, citrus peel, etc. Spent botanicals, therefore, contain the botanical residue after gin production, and its composition will vary depending on the type and proportion of the botanicals used. Reportedly, about 30 to 40 pounds of spent botanical is generated for every batch of gin (750 – 1000 litres) produced making it the major by-product of gin distillation. The conventional management protocol for spent botanicals in most distilleries is its utilisation by farmers as compost. However, the present socio-economic dynamics and increased awareness on resource use by both producers and consumers means that there could be additional added value uses for distilled gin spent botanicals.

9. Conclusion

Beer and spirits have prominent shares in the alcoholic beverages market with their demand and popularity predicted to grow exponentially. This means a constant and growing output of brewing and distilling by-products and an opportunity to harness them for added value uses. With production economies shifting towards sustainable production practices, this review study has given an insight into novel valorization initiatives for these by-products. There are several studies that have explored different aspects of wastes and by-products value addition and applied them to brewing and distilling by-products in product development and raw materials for industrial applications. Spent grain which is predominantly used as animal feed is now being explored for biofuels production, bioactive ingredients extraction, sustainable packaging, substrate in fermentation and anaerobic digestion, and even as an adsorbent. Spent yeast has been studied for its ability to enhance some functional properties in foods, bioactivity and functional food applications, fermentation supplement, enzyme source and yeast extract. Pot ale has great potential in the quantity of lactic acid that could be extracted from it and, it is a valuable substrate in anaerobic digestion. Other by-products materials – trub, spent kieselguhr and CO_2 have been explored for added values in biorefinery, packaging, and other applications. Spent botanicals which is the by-product of gin distillation requires more studies to obtain information on its chemical profile and performance in added value uses.

On a global scale, demand for high quality food ingredients is on the increase. There are several national and international policies focused on fostering high levels of innovation and practice in the food industry and other associated sectors for new product development in nutraceuticals and functional foods. Attention is being drawn towards valorisation of different by-products of the food industry for value addition such as obtaining bioactive hydrolysates and proteins. Some of the reasons for this high interest

in by-products derived ingredients include but not limited to climate change, increasing resource efficiency, and development of new strategies for sustainable production practices. While significant progress has been made from the shift from land spread and animal feed to these novel initiatives, its adoption by the sector in managing of the by-products is still limited. Recent studies still show that animal feed remain the main management practice for brewing and distilling by-products. There is an opportunity for standardisation and commercialisation of some of the initiatives to provide a pathway for their implementation and integration into product streams.

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Declaration of interest statement

The authors report no conflict of interest.

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Table 1. Conventional management practices for brewing and distilling by-products.

By-product	Management practice
Spent grain	Spent grain is predominantly used for animal feed either directly or in combination with other feed materials. Other management practice for spent grain is ensiling for use as silage, composting, and land spreading.
Spent yeast	Spent yeast is mostly disposed as effluent with or without on-site treatment. In some cases, it is dewatered and in animal feed.
Trub	Trub is mostly discharged as effluent. However, it can also be dewatered and added to animal feed or used as soil conditioner.
Spent kieselguhr	Spent kieselguhr is either disposed as effluent (when small amounts are generated), sent to landfill (for large quantities) or used as a soil additive.
Pot ale	Pot ale is either disposed to sea/river (for licensed distilleries) or land spread on farmlands. Some distilleries concentrate their pot ale (pot ale syrup) which is then incorporated either into raw draff/straw or dark grains for animal feed.

Based on Shaiith (2015)

Table 2. Chemical composition of major brewing and distilling by-products.

						References
Spent grain (d.m.)						
Moisture	**Ash**	**Crude protein**	**Lipids**	**Total fibre**		(Chetrariu & Dabija,
5 – 8%	1 – 5%	14 – 30%	3 – 10%	50 – 70%		2020; Mitri et al., 2022).
Spent yeast						
Moisture	**Dry matter**	**Ash**	**Crude protein (d.m.)**	**Lipids**	**Carbohydrates**	(Rachwał et al., 2020;
74 – 86%	10 – 16%	2 – 8.5%	40%	1%	59%	Thammakiti et al., 2004)
Trub (d.m.)						
Bitter components	**Ash**	**Crude protein**	**Lipids**	**Phenolics**	**Carbohydrates**	(Sterczy´nska et al.,
7 – 32%	5%	40 – 70%	1 – 8%	20 – 30%	4 – 8%	2021)
Pot ale (d.m.)						
Dry matter	**pH**	**Crude protein**	**Yeast**	**Total phosphorous (d.m.)**		(White et al., 2020)
5.1%	3.9	33%	2.9×10^8 cells/mL	13.4 g/kg		

Table 3. Estimated lactic yield from pot ale across major whiskey producing countries.

Country	**Estimated lactic acid in pot ale (Kilo tonnes)**
India	1034
Scotland	607
North America	368
Japan	99
Ireland	71
Total	**2181**

Based on McNerney (2019)

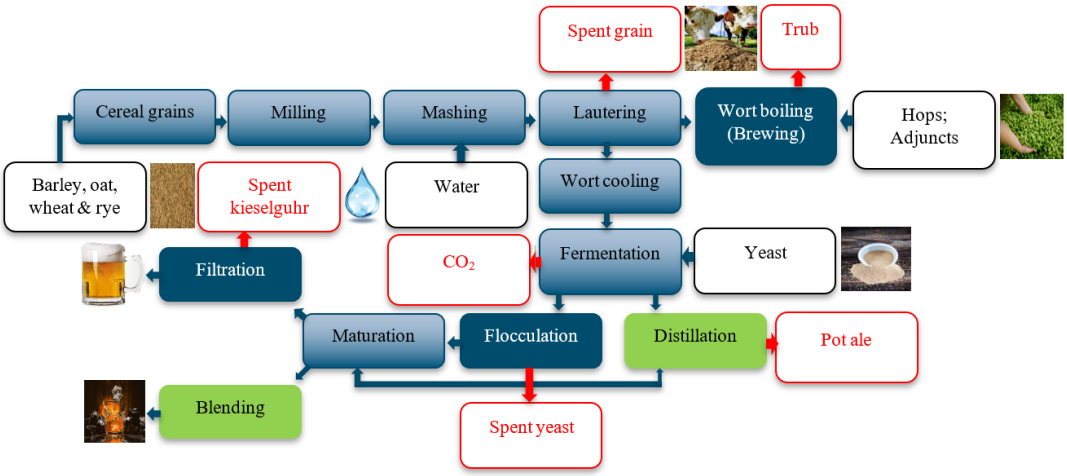

Figure 1. Unit operations in brewing and distilling showing the different inputs and by-products materials.

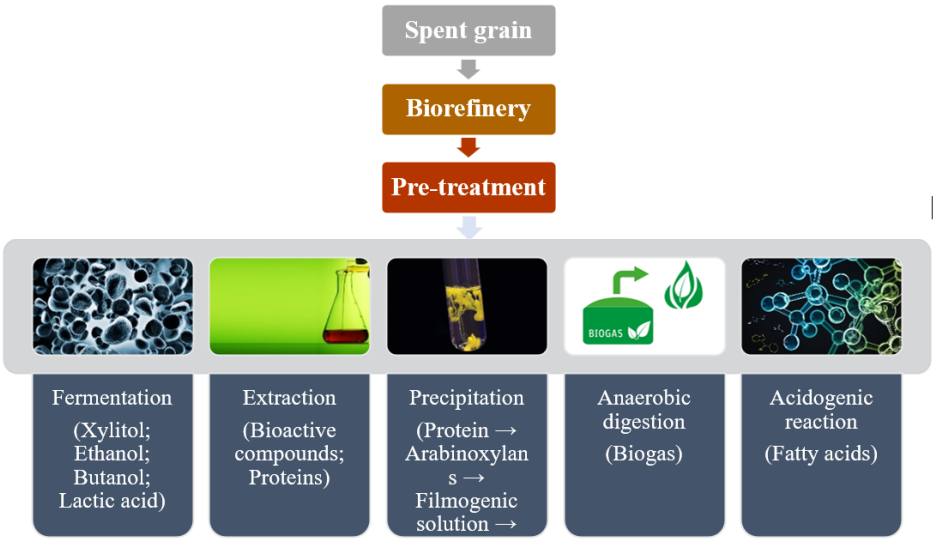

Figure 2. Overview of technological routes of spent grain in different biorefinery processes. Based on Sganzerla et al. (2021).

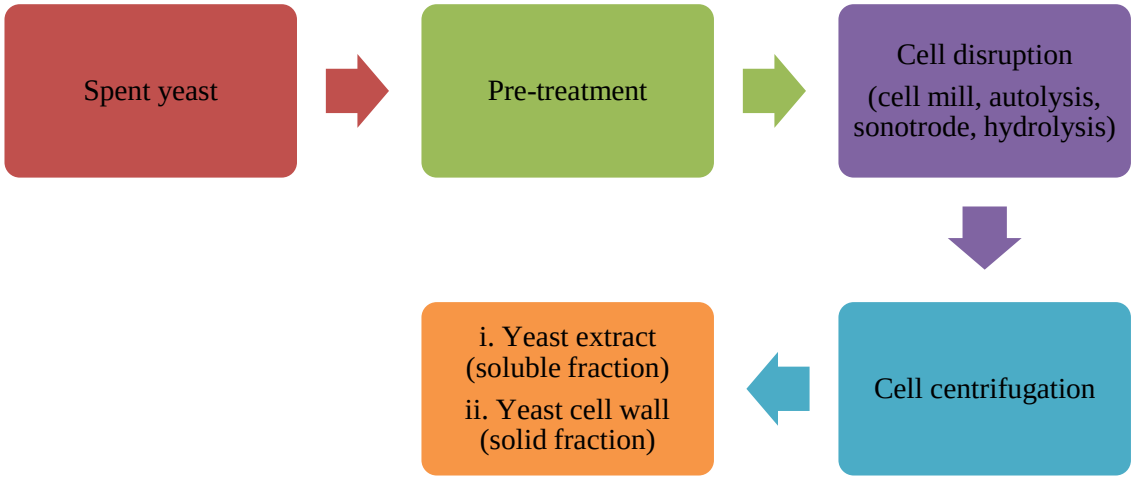

Figure 3. Steps involved in the production of yeast extract from spent yeast.

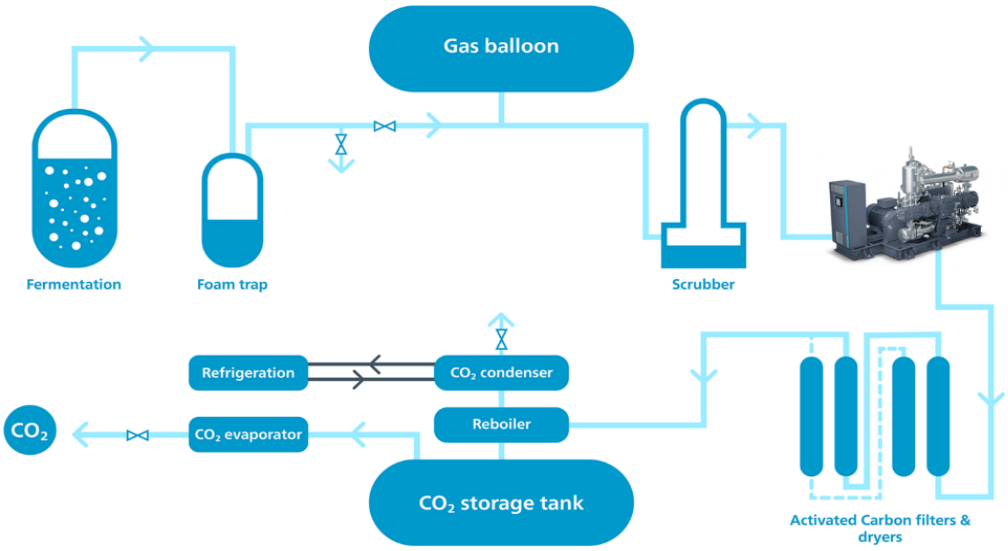

Figure 4. CO_2 recovery process from fermentation. Based on Atlas Copco (2022)