



Article

Sustainable Strategies for the Recovery and Valorization of Brewery By-Products—A Multidisciplinary Approach

Alina Soceanu ¹, Simona Dobrinas ^{1,*}, Viorica Popescu ¹, Alina Buzatu ² and Anca Sirbu ³

- Chemistry and Chemical Engineering Department, Faculty of Applied Chemistry and Engineering, "Ovidius" University from Constanta, 900470 Constanta, Romania; asoceanu@univ-ovidius.ro (A.S.); vpopescu@univ-ovidius.ro (V.P.)
- Romanian Philology, Classical and Balkan Languages Department, Faculty of Letters, "Ovidius" University from Constanta, 900470 Constanta, Romania; alina.buzatu@univ-ovidius.ro
- Department of Fundamental Sciences and Humanities, Constanta Maritime University, 900663 Constanta, Romania; anca.sirbu@cmu-edu.eu
- * Correspondence: sdobrinas@univ-ovidius.ro; Tel.: +40-241606434

Abstract: The prevention of environmental pollution is a current concern of the population, which is looking for ways to reduce the production of industrial waste. The brewing industry generates huge amounts of waste, with difficult management from an economic point of view. The waste obtained from the technological process of beer production is used in various branches, such as the food industry, mainly as feed, additives, or food ingredients; as animal feed; in biofuel production; and in building or packaging materials. The valuable by-products obtained from brewery waste can serve as raw materials for further processing or become functional ingredients for the production of new functional products. Reusing and recycling are essential strategies for transforming waste into new valuable resources, and such strategies enable circular solutions to maintain the value of products and resources for as long as possible. The chemical composition of the waste obtained from beer manufacturing can vary slightly depending on the type and quality of the ingredients used and the prevailing conditions during each stage of the manufacturing process. This paper focuses on sustainable strategies for the recovery and valorization of brewery by-products. Experimentally, the aim was to determine the chemical characteristics of different types of brewery waste, such as moisture content, ash, pH, total content of phenolic compounds, and total protein content. The experimental values obtained have shown that brewery waste is a valuable by-product.

Keywords: waste; brewery; antioxidants; phenolic compounds; sustainability; strategies



Citation: Soceanu, A.; Dobrinas, S.; Popescu, V.; Buzatu, A.; Sirbu, A. Sustainable Strategies for the Recovery and Valorization of Brewery By-Products—A Multidisciplinary Approach. Sustainability 2024, 16, 220. https://doi.org/10.3390/su16010220

Academic Editors: Dario Donno and Dimitris Skalkos

Received: 9 December 2023 Revised: 21 December 2023 Accepted: 24 December 2023 Published: 26 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Beer is a special drink; it has been known since 6000 years ago, from the time of the Sumerians. At that time, it was a divine drink intended only for the Goddess of Fertility, and later, it was used by monks in the Middle Ages as a sweetener for meat, being considered a food rich in carbohydrates, proteins, vitamins B1, B6, B12, PP and E, folic acid, nicotinic acid, potassium, magnesium, etc. Moderate consumption of beer has a beneficial effect on human health mainly due to antioxidants, suppression of the rise of blood plasma lipoproteins [1], anti-inflammatory effects, and reduced risk of cardiovascular disease [2–4]. In beers, a considerable part of the antioxidant capacity is linked to the content of phenolic compounds [5].

Beer is one of the most popular alcoholic beverages in the world. It is undistilled and obtained by fermentation in the traditional way with only four basic ingredients: water, wort (made from malt), hops, and yeast; the malt can be partly replaced by unmalted grains (corn, barley, or rice) or possibly with some enzymes. Barley malt is usually used in brewing, which, when wort is obtained, provides both the enzyme equipment and the

Sustainability **2024**, 16, 220 2 of 12

substrate necessary for enzyme action and, at the same time, gives finished beers a typical malt flavor.

The classification of the types of beer denotes the character, even the origin of this drink, the ingredients used, and also the manufacturing technique, giving clear clues in terms of taste, appearance, color, and smell of beer. The aroma, color, and texture of beer may differ depending on the type of fermentation, which may be low or high frequency. Based on the types of fermentation, two main types of beer are distinguished: Lager beer, obtained by a low fermentation process, and Ale beer, obtained by high fermentation. Apart from the main types of beer mentioned, there are other types, such as: wheat beer, spontaneous fermentation beer, non-alcoholic beer, or craft beer. Of course, there are other classifications of the types of beer established according to the ingredients used in the production or certain particular characteristics of the brewing process, and this is the case with the types of hybrid beer. Beer assortments also differ depending on the brewer's recipe.

However, there is a global trend in the production of new types of beer, known as "styles", that differ from traditional ones. Beer styles vary significantly due to wort changes in the production technology through different microorganisms used, the use of atypical malts, or the addition of various adjuvants such as salt, herbs, or spices. The use of fruits in beer production is one of the most prominent trends found globally in local craft breweries or industrial breweries [6,7].

Modern brewing technologies that take into account technical, economic, sanitary, and quality standards have emerged. The implementation of unconventional technologies in the technological process of beer manufacturing aims to simplify technological operations, reduce production costs, reduce manufacturing time, diversify beer assortments, as well as reduce the amount of waste resulting from the technological flow [8,9].

The use of synthetic antioxidants in the food industry is restricted by legislation [10]. For this reason, a sustainable and renewable alternative is to obtain these compounds from waste materials, such as agroindustrial residues, plants, vegetables, and fruits, which are efficient sources of phenolic compounds [11–14].

2. Product Identity and Sales Strategies

If the scientific discourse of chemistry addresses beer in terms of denoted, clear, transitive, non-ambiguous, measurable information, talking about ingredients, properties, technological processes, etc., it is interesting to see how, having become a commercial product, beer becomes the pretext for fictional constructions, stories with legitimizing value.

Product identity, chemical composition, and sales strategies are some factors that can influence beer consumers [15].

Its commercial product status is known to entail a hybrid identity, codified by both image and written word. A product's labels become a semiotic space in which, on the one hand, expert, mandatory, legally regulated information (type of beer, ingredients, proportions, etc.) and, on the other hand, advertising information and telling a story, place the commercial product in a fictional world, attaching experiences and values projected by the imagination. Beer brands devote considerable financial and creative resources to building these stories—because they sell alongside the product and also sell the product—in fierce competition. To be recognizable and easy to remember, stories have semantic-symbolic labels, which are both iconic (the brand image) and textual—short, concise, simple, sometimes striking slogans, often delivered in a certain manner because the intonation or rhythm of delivery increases the chances that the prospective buyer will remember the product and be persuaded to buy it. There is another essential feature of these stories that are attached to a product through advertising discourse—they always add positive qualifiers to a product because they are meant to legitimize it in the commercial markets by enhancing its value.

The best-known local beer brands build their identities through often comparable advertising strategies. Most of them advertise premium quality and the fact that they

Sustainability **2024**, 16, 220 3 of 12

are produced in Romania. Existence for several years adds value; some brands boast a foundation dating back to 1718 or 1874, another claims existence since 1974, and craft beer brands show more recent entry into commercial markets.

Image emblems symbolically link beer brands to Romanian identity, building advertising fictions around animals or birds that are representative of the local fauna—the brown bear, the bearded vulture, etc.—which imply strength, robustness, superiority, and royalty. The texts on the label enhance the image emblems through identity emotion, giving value to the commercial story by over-emphasizing a characteristic that is always positive; one brand with an animal emblem defines itself as the king of beer in Romania, another says that the story goes further, accompanying the message with the image of the national flag.

Other image emblems seem to highlight the production process itself as a guarantee of quality; a representation of the brewery appears on the label, which is called—also in the official, registered name—"the good beer brewery". Another brand also adds to its label the image of a building without any other text specifications, leading us to believe that it may be the production site or another space (a house?) that conveys to the buyer the idea of community, conviviality, and shared well-being.

Regardless of the strategies of advertising persuasion and the stories through which they assert their identity, local beer brands insist on communicating that they are part of our lives and that they share our experiences by responsibly facilitating joviality, euphoria, friendship, communication, and humor.

Expert information chimes with advertising fiction: some aimed at communities with scientific expertise, others at the general public. As with humans, a product's identity is part hard, denoted, verifiable information, part imaginative projection, an illusion of reality or make-believe.

3. Brewery Technology

In recent years, the beer industry has recorded important progress worldwide in terms of technology and the provision of new types of equipment and installations [16,17]. The technological flow is fully automated, monitored, and controlled from the "command and control room", where there are computers containing special programs for monitoring the entire technological process of brewing beer.

The classic technological process of beer manufacturing consists of obtaining malt, which is realized through the following sequence of phases: cleaning, sorting, weighing, germination, drying, and root cleaning of barley grains; obtaining the beer wort is achieved by grinding, scalding, saccharification, filtering the scald, boiling the malt wort with hops; primary fermentation and secondary fermentation; and final operations include filtration, pasteurization, and bottling.

3.1. Raw Materials

The malt represents the main raw material for brewing beer and is obtained by germinating barley seeds in order to obtain the source of hydrolytic enzymes, which, through their action on the substrate, determine the formation of the extract. The quality of the beer is due to the quality of the malt, which is why it is also called the "soul of beer".

The hops are the indispensable raw material; they represent the "seasoning of beer", giving it the bitter taste, specific aroma, color, clarity, improvement of the foam, and preservation power of the beer (natural preservative), which it influences thanks to the compounds that it contains, especially bitter substances (resins \sim 12–21%) and essential oils 0.5–2.5%.

The water must be drinkable because, following the technological flow of obtaining beer, it has a contribution of approximately 88% and requires a certain content of salts not to influence the technological process. The hardness of the water depends on the type of beer, and the pH of the wort and beer is influenced by the composition of the water [18].

Sustainability **2024**, 16, 220 4 of 12

3.1.1. Unmalted Cereals

Unmalted cereals are used to obtain a lighter-colored beer with abundant and stable foam: maize is used in the form of flour in a proportion of 5–30% compared to the amount of malt; rice is used to obtain bottom-fermented blonde beer by separately processing barley and rice bran mixed at 65 $^{\circ}$ C; barley, oats, and wheat are used in special types of beer.

3.1.2. Yeast

The yeast used in the technological flow of beer production is part of the *Saccharomyces carlsbergensis* group, which always ferments alcoholically. It was derived either from pure laboratory cultures or from the recovery of cells grown from a previous batch of fermentation. The most important property of yeast is its ability to agglutinate. From a fermentation point of view, yeast can be: top fermentation yeast, which ferments at high temperatures (greater than $10\,^{\circ}$ C) and rises to the surface at the end of fermentation, or lower fermentation yeast, which ferments at low temperatures and settles to the bottom of the yessel at the end of fermentation.

3.2. Stages of the Technological Process of Brewing Beer

Following the qualitative and quantitative reception of the malted and unmalted cereals, they are sent for cleaning, weighing, and removal of impurities, which is done through a magnetic separator or with six-roll mills. After that, the malt is ground so that the enzymes can act in the fermentation and saccharification stages, transforming the insoluble macromolecular substances into soluble products that will enter the composition of the beer wort.

Grinding the malt is a relatively long process, determined not only by the size and quality of the grain but also by the temperature of the water used. In order for the milling process to be efficient, the malt must undergo the polishing process to slide easily into the mill, avoiding adhesion to the walls of the soaking bunker.

Malting and saccharification form a complex process of enzymatic hydrolysis and consist of mixing ground malt with unmalted cereals and water, where the malt enzymes will destroy flour components and nitrogen-assimilable substances will accumulate in the must, forming brazing. The amount of water used is variable and is added depending on the type of malt used. As a result of this process, the disaggregation of proteins and the transformation of starch into dextrin and maltose are obtained [19].

The next stage is the filtering of the lees, which aims to obtain the beer wort and takes place by separating the wort from the insoluble parts that will later form the malt wort. In the first phase of the process, the must will flow freely with the formation of the first must, and in the second phase, the wort will be washed with water (50–75 $^{\circ}$ C) in order to recover the retained extract.

Boiling the wort with hops is the stage obtained after filtering the lees with the addition of hops and aims to solubilize the bitter and aromatic substances of the hops, protein coagulation, enzyme inactivation, and must sterilization, concentration and coloring of the must, cooling and clarifying the must, and elimination of some sulfur substances.

After boiling the wort and separating it from the hops, it is necessary to cool and retain the wort so that the temperature is brought to the values at which the seeding with yeast cultures is done. It is a complex process that takes place in the presence of air; it causes chemical transformations as a result of the oxidation of maltose, glucose, protein substances, etc.

The cooling of the wort takes place in two stages: the first time, there is a pre-cooling from $100~^{\circ}\text{C}$ to $65~^{\circ}\text{C}$, followed by a deep cooling that must reach the yeast seeding temperature of $6\text{--}18~^{\circ}\text{C}$.

The hot wort is formed in the boiling step of the wort with hops and separates in the pre-cooling step. It consists of coarser particles (30–80 μ m) and is removed from the must by sedimentation, centrifugation, or settling cyclones.

Sustainability **2024**, 16, 220 5 of 12

The cold tube is formed during deep cooling after the hot tube has been separated. It consists of fine particles, and its separation is done at a maximum percentage of 80–85% by sedimentation, centrifugation, or flotation.

Sterilization of the must is done by inactivating the foreign microflora that occurs during the uncontrolled acidification of the must. It is sterilized by bringing the must to the boiling stage. In order to be seeded, the must is cooled to $6-7\,^{\circ}$ C, to which the yeast suspension is added, obtained through pure laboratory cultures. There is also bubbling with purified air to stimulate fermentation.

After all the primary wort phases of the technological flow and its fermentation, the young beer product is obtained. Fermentation can be of two kinds: primary and secondary.

The primary fermentation takes place in several stages, and the result is young beer (fermentable extract of 1.5%). Young beer is characterized by an unpleasant taste and aroma due to secondary fermentation products, contains insufficient CO_2 , and is slightly cloudy due to the presence of yeast or other suspended particles.

Secondary fermentation helps primary fermentation obtain a finished product with pleasant organoleptic qualities for consumption. It takes place slowly, where the rest of the fermentable extract is transformed into alcohol and CO_2 and is called maturation or storage. The duration of the secondary fermentation can be reduced by stirring the must, fermentation under pressure, or fermentation in bioreactors. If, toward the end of the secondary fermentation, the beer remains cloudy, it means that the yeasts are wild or some bacteria are present. Cloudy beer resulting from secondary fermentation can be clarified with the help of substances such as tannins, bentonite, silica gel, activated carbon, enzyme preparations, reducing substances, polyamides, etc.

Beer, as a finished product, is distributed in glass bottles, tinplates, or aluminum and stainless-steel barrels. Regardless of the packaging method, the beer is packaged isobarometrically (equal pressures in the tank and in the packaging). The bottling technological process takes place with the help of machines that can be simple or complex, automated or semi-automated [20,21].

3.3. Sustainable Strategies for Recovery and Valorization of Brewery Waste

"Waste" from the beer industry represents any substance obtained as a result of the technological process that the holder eliminates, intends to eliminate, or has the obligation to eliminate.

Due to its complex chemical composition, the waste resulting from the processing of food products generally presents optimal conditions for the appearance and development of numerous microbiological and biochemical processes, which ultimately lead to their total degradation. For this reason, it is necessary to first take measures to ensure the conservation of waste until the moment of its subsequent use or processing.

Following the technological flow of obtaining beer, waste results can be used in the manufacturing process of other products in different industries, such as: the pharmaceutical industry, the chemical industry, or the animal feed industry.

The waste resulting from beer production is part of the category of non-hazardous production waste, being classified into specific waste and non-specific waste (packaging, containers for storing chemicals used in the cleaning and disinfection of facilities).

Spent grains or brewer's spent grains (BSGs) represent approximately 85% of all residues produced by the brewing industry. BSG is the solid residue left after filtration of the beer wort, a by-product obtained after the saccharification of the malted cereal grains [22,23]. These are formed at the beginning of the brewing process and are removed before the boiling step. This solid residue is composed of barley hulls, the husk pericarp, and seed coat. This is a heterogeneous material formed from lignocellulosic biomass and is rich in protein (20–30%), fiber (30–70%), lipids, vitamins, and minerals. It contains approximately 12–28% lignin, 12–25% cellulose, and 28% non-cellulosic polysaccharides, mainly arabinoxylans. Spent grains have been proven to contain vitamins, minerals,

Sustainability **2024**, 16, 220 6 of 12

and many amino acids. This by-product is also rich in oligo- and polysaccharides and phenolic compounds.

Recycling strategies for BSG were identified in the literature as animal feed, human food, composting, biogas, substrate for mushroom production, absorbents, ceramic material, paper, bricks, bioethanol, and food packaging [24,25].

Wet, spent grain can serve as feed for ruminants; the high moisture content makes it easily digestible for animals [26]. Dried spent grains are also an alternative protein source for ruminants and have a positive influence on production efficiency in cattle without affecting fertility. It improves the production and composition of milk and increases the fat and protein content [27,28]. The addition of spent grain to a lamb's diet has been found to have a positive effect on its growth performance and meat quality [12,29].

BSG represents an innovative source for the food industry that can improve the value of food products, such as snacks, bread, pasta, cereals, sausages, or meat patties [30,31], mainly because of its health-related bioactive components: alkaloids, antibiotics, plant growth factors, food-grade pigments, and phenolic acids [12,32].

Composting is another interesting alternative to BSG because it is a rich source of nitrogen and organic materials for soil nutrition. A sustainable strategy that brings advantages to the problems involving climate change issues is biogas generation from the conversion of organic brewery waste. The biogas can be reused for energy generation in the brewery. The use of BSG as a by-product for the generation of substrate for mushroom production or to produce heavy metal absorbers or ceramic materials has been successfully tested. Bioethanol is also a product that can be obtained from malt bagasse [25].

There is a great demand for biodegradable materials for food packaging applications, and BSG is an ideal resource for sustainable food packaging because of its components, such as cellulose, lignin, AX, and protein [24].

Malt tusks are obtained following the germination stage of malt, and the correct name is malt radicele. The removal of the tusks takes place even after the drying stage because the very dry state of the malt tusks allows for easy detachment by rubbing the grains with each other and by hitting them against the walls of the machine. Malt tusks are used for fodder purposes and for the composition of culture media in the compressed yeast industry. For cattle feed, malt tusks are used mixed with coarse fodder (chaff, straw). This feed is not eaten with pleasure by animals because of its bitter taste. It is recommended to be used in the feeding of dairy cows, as it favorably influences milk production.

Having a high content of nutrient substances such as vitamins, provitamins, and other growth stimulants, they are used to prepare molasses for the manufacture of fodder yeast and to manufacture lactic acid by fermentation [33].

Lately, research has shown that the methanolic extract of malt tusks is an effective antioxidant and that, due to its low price, it could constitute a rational capitalization of this waste from breweries [14]. The use of malt tusk extract or flour as an antioxidant is of particular importance in the food industry, firstly due to its lack of harmfulness compared to other antioxidants, and secondly, due to its high content of protein substances, vitamins, a favorable flavor for some preparations, and the color and content of certain enzymes that may be valuable for some foods. Malt tusk flour is used in various pastries. It has also yielded good results in the preservation of peanut oil, butter, and margarine. The malt tusk has the form of thin grains of yellowish-brown color, containing vitamins of the B complex, vitamin E, provitamins A and D, as well as other growth stimulants.

Treating the wort or beer with this extract from malt tusks leads to an increase in the physico-chemical stability of the beer. The treated and pasteurized beer has a stability 2–3 times higher than the untreated one [14].

Malt wort is the one that results in the highest quantity from the technological process of brewing, being the result of the filtration stage of the wort at the boiling section. The resulting malt wort has a humidity of about 80%, with a sweet taste and the smell of malt.

Beer wort is a special fodder for feeding animals and, in particular, dairy cows. However, it can only be used on a large scale in its fresh state because, after a relatively short

Sustainability **2024**, 16, 220 7 of 12

storage time, as such, it undergoes butyric fermentation, which produces an unpleasant smell, so that the animals refuse to consume it or do not consume it with pleasure.

Its silage in special cemented basins must be done carefully. If the fodder is made with wort that has undergone butyric fermentation, the taste of butyric acid is also transmitted to the milk, thus making it unfit for consumption.

To preserve the wort for a longer time, it can be dried, which requires additional fuel consumption but ensures the long-term preservation of its fodder qualities and facilitates long-distance transportation.

The wort contains an appreciable amount of protein and non-hydrogen extractive substances, which gives it a high nutritional value for the manufacture of animal feed. The wort contains 70–75% of the fat and protein of the malt used in the brewing process. It has important forage value.

Besides its use as fodder, the wort has also found use as an addition to pickling polished cast iron. The wort, after treatment with hydrochloric acid, is used in pickling solutions at a concentration of 10–12 g/L [20,21].

Hop wort results from boiling the wort with hops. After boiling the beer wort together with the hops, it is pumped into the hop separator. The hop pulp, according to its components and the degree of assimilation (50%), corresponds to the meadow hay. To date, it has not found use as fodder due to the fact that it has a strong bitter taste, and the cattle refuse to consume it as such.

Animal feeding experiences with mixed waste (hops and malt) proved not only that the waste is suitable for feeding cattle but also that it exerts a favorable effect on their weight gain as well as on the quantity and quality of milk obtained.

Due to its chemical composition, which is similar to that of manure, hop wort can be used as fertilizer in agriculture [20,21].

Protein sediment (Hot Trub) is a by-product obtained mainly in the separator after the brewing process. It consists of hops, inactive yeast, fat, and protein.

The protein sediment appears in the beer wort after boiling with hops, continuing in the cooling phase. Its separation begins with the removal of the hop cones, where a part is retained on them, but the greater part accompanies the wort until the cooling phase. Here, following the cooling process, another part of the protein precipitates and is also separated. The protein sediment is found as large flakes (coarse trub) or in the form of small particles, known as fine trub. The more or less complete separation of the dregs from the beer wort depends on the equipment and operations used in the cooling phase. The amount of wort obtained depends on a whole series of factors, including the quality of the malt, the grinding degree of the wort, the amount of hops used, the concentration of the wort when boiling with hops, the duration and intensity of cooling, etc.

The chemical composition of hot trub is very varied. It contains albuminoid substances, tannins, hop resins, and mineral substances. The highest percentage is represented by albuminoid substances. The ethereal extract includes not only fats but also bitter substances from the hops, which give the protein sediment its bitter taste, which prevents its direct use as feed, although the degree of assimilability, in general, is quite high.

The protein sediment, as such, can be used primarily as feed but only as an addition in small quantities to other feeds. In this way, it can be added to the malt wort from boiling. It is also used to feed fish in ponds, as a binder in road works, or as fertilizer [20,21].

The foam layer from fermentation is formed in the primary fermentation process of beer wort and is composed of hop resins and precipitated protein substances.

Before passing the young beer to secondary fermentation, the layer formed on the surface of the beer is carefully removed because the bitter resins that it contains would render the beer too bitter and unpleasant a taste. Although the foam layer, which accounts for 0.2% of the beer, is not yet used, it was concluded that, as with the protein sediment, extraction of the hop resins with organic solvents is possible. With the extract obtained, approximately 20% of the fresh hops used in beer production can be replaced. The extract

Sustainability **2024**, 16, 220 8 of 12

obtained from the foam layer contains 14% more hard resins compared to the extract obtained from fresh hops when benzine is used as a solvent.

Almost all the bitter substances were removed from the foam layer by extraction. The high content of digestible proteins shows that, after the removal of bitter substances, the residue can be used as feed.

Residual spent yeast or brewer's spent yeast (BSY) results in the form of waste in beer manufacturing, both from the fermentation tanks (primary fermentation yeast) and from the storage tanks (secondary fermentation yeast). The main shortcoming in relation to baker's yeast or fodder yeast is the pronounced bitter taste due to the hop resins it contains. Due to its valuable principles, brewer's yeast is used, as such, or after a preliminary drying process, in animal husbandry as a component of concentrated fodder.

In its wet form, as it results from beer production, yeast is extremely degradable: at ambient temperature, it enters a degradation process after a few hours. If it is dehydrated so that it reaches a moisture content of less than 10%, it can be stored without deterioration for a very long time [20,21].

4. The Chemical Characteristics of Different Types of Beer Waste

BSG hot trub and residual spent yeast samples were collected from a brewery located in the Region of Dobrudja, Romania. The studied samples were collected immediately after their generation in the brewing process stages for the production of traditional lager-type beer—the brewery spent grain after lautering, the hot trub after wort boiling, and residual spent yeast after the yeast fermentation step (Figure 1) [34]. All used reagents were of high grade and purchased from Sigma Aldrich or Merck.

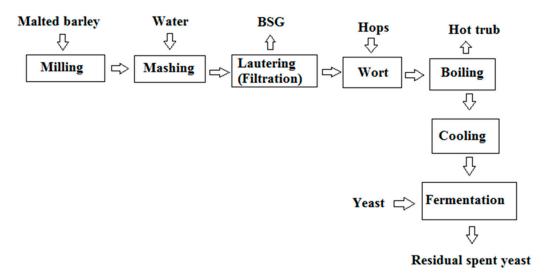


Figure 1. Steps of the brewing process to obtain the most important by-products.

The determination of moisture content, ash, pH, total content of phenolic compounds, and total protein content was aimed. Thermal drying was used for the determination of the moisture content of the studied samples. The moisture content was determined as the difference between the weight of studied samples and the weight recorded after 1 h and 30 min heating at 130 °C in an oven. Ash content was made by calcination in a muffle at 700 °C. The pH was measured with a pH meter. Total protein content was determined by the Kjeldahl method. The method consists of the mineralization of the sample with concentrated sulfuric acid when the nitrogen from the organic combinations is released and passed as ammonium sulfate. Reaction with a strong base releases ammonia, which is removed from the solution by distillation and captured in an excess solution of 0.1 N sulfuric acid. The total protein content was determined using the Kjeldahl system consisting of the Turbosog and Vapodens apparatus.

Sustainability **2024**, 16, 220 9 of 12

Extraction of phenolic compounds in studied samples was conducted in 80% methanol for 2 h at room temperature, then the extracts were centrifuged, and the supernatant was retained and stored at $-20~^{\circ}\text{C}$ until analysis. Total phenolic content was determined using the Folin–Ciocalteu method [35], and the results were expressed as mg gallic acid equivalents (GAE) per 100 g of studied sample. Aliquots of 0.5 mL extracts were mixed with 1 mL of 1:2 (v/v) Folin–Ciocalteu reagent in 50 mL calibrated flasks. Then, 1 mL ethanol and 1 mL sodium carbonate solution (20%) was added. The solution was vigorously mixed, allowed to react for 10 min at room temperature, and filled up to the mark with distilled water. The resulting mixtures were maintained at room temperature for 30 min, and the absorbance was measured at 675 nm against the corresponding blank with a UV-VIS spectrophotometer (Jasco 550). Quantification was performed by a calibration curve using gallic acid as a phenolic standard ($R^2 = 0.9997$, y = 0.0041x).

5. Results and Interpretations

Table 1 presents the experimental values obtained for the studied samples of the brewery waste.

Table 1. Values of the moisture content, ash content, pH, total protein content, and total content of phenolic compounds of the studied samples.

| Samples | Moisture Content, % | Ash Content, % | pН | Total Protein Content, % | Total Content of Phenolic Compounds, mg GAE */100 g dw ** |
|-----------------------------|---------------------|----------------|-----|-----------------------------|-----------------------------------------------------------------|
| Brewer's spent grains (BSG) | 5.4 | 4.1 | 5.1 | 17.46 | 354.26 |
| Hot trub | 5.8 | 5.3 | 4.5 | 12.37 | 285.35 |
| Residual spent yeast | 7.6 | 15.1 | 4.4 | 34.38 | 112.45 |

^{*} GAE = gallic acid equivalents. ** dw = dry weight.

For the studied samples, pH values ranged between 4.4 and 5.1; the highest value was obtained for the brewer's spent grains. Ash content is related to mineral content, and for the studied samples, values were between 4.1 and 15.1%; the highest value was obtained for residual spent yeast. The ash content of residual spent yeast was in agreement with the value reported by Vieira et al. [36]. For the studied samples, the moisture content was between 5.4 and 7.6%. The highest protein content was obtained for residual spent yeast (34.38%), while the lowest value was obtained for hot trub (12.37%).

The phenolic compounds in beer originate mainly from beer ingredients used in the brewery process; phenolic acids and flavonoids are the most studied in beer [37]. Brewery wastes like spent grain, hot trub, or residual spent yeast are also valuable byproducts thanks to their phenolic composition. Results showed that the total phenolic compound content in the brewer's spent grains was 354.26 mg GAE/100 g dw, in the hot trub was 285.35 mg GAE/100 g dw, while in the residual spent yeast, it was 112.45 mg GAE/100 g dw. A decrease was observed in the total phenolic compounds that can be associated with the precipitation of compounds during the maturation process or their adsorption to the hot trub during processing or to the yeast cells during the fermentation process [38]. These phenolic compounds are considered natural antioxidants with effects on human health, such as cardiovascular diseases, neurogenerative diseases, diabetes (types I and II), and some types of cancer [14,39].

An efficient way of stabilizing beer is to reduce the polyphenol content by adsorption with polyvinylpolypyrrolidone (PVPP), which forms hydrogen bonds between the hydroxyphenolic group and the amide of PVPP. After use, the PVPP resin is regenerated in the brewery, in a washing process that generates large quantities of a waste stream, which contains large amounts of polyphenols, being a promising alternative and economical source of natural antioxidants. The main phenolic compounds present in the crude extracts

Sustainability **2024**, 16, 220

are simple phenolic compounds, mainly phenolic acids and flavan-3-ol catechin, which are the main causes of beer haze [14].

Sustainable strategies that valorize by-products from brewery processes are more convenient than expenses attributed to the disposal of industrial by-products or waste treatment costs [12,40,41]. Brewing waste is used mainly as animal feed, in biofuel production, building, or packaging materials [42]. The recovery of proteins and polyphenols from brewing wastes may represent an innovative source for the food industry and biotechnological processes. An adequate approach that emphasizes the value of brewing industry wastes is to provide knowledge about chemical composition, marketability, and research implications [34].

Brewery waste is a negative cost factor for the brewery industry; its rich content of complex carbohydrates, nitrogen, and minerals is very important to the production of biotechnological products such as biofuel, enzymes, organic acids, and bioactive compounds [43].

6. Conclusions

The use of green technologies, the exploitation of food industry by-products, and outside-the-box thinking are sustainable strategies to reduce the pollution arising from industrial activities. The concept of zero waste means implementing a circular economy, where companies should not consider residues as waste but as raw materials for their use in other processes or to valorize these by-products as functional ingredients to create a sustainable food system. This concept also means to transform society by changing resource management, influencing consumer behavior, and creating the appropriate legal framework and economic incentives.

Author Contributions: Conceptualization: A.S. (Alina Soceanu); data curation: A.S. (Alina Soceanu), S.D., A.B. and A.S. (Anca Sirbu); formal analysis: V.P.; investigation: A.S. (Alina Soceanu) and V.P.; methodology: A.S. (Alina Soceanu), S.D., A.S. (Anca Sirbu), A.B. and V.P.; project administration: S.D., V.P. and A.S. (Anca Sirbu); software: A.B.; supervision: V.P.; validation: S.D.; visualization: A.S. (Alina Soceanu) and V.P.; roles/writing—original draft: A.S. (Alina Soceanu), S.D. and A.S. (Anca Sirbu); writing—review and editing: A.S. (Alina Soceanu), S.D., A.B., A.S. (Anca Sirbu) and V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Rozsypal, J.; Sevcik, J.; Bartosova, Z.; Papouskova, B.; Jirovsky, D.; Hrbac, J. Automated electrochemical determination of beer total antioxidant capacity employing microdialysis online coupled with amperometry. *Microchem. J.* 2022, 183, 107955. [CrossRef]
- 2. Chiva-Blanch, G.; Magraner, E.; Condines, X.; Valderas-Martínez, P.; Roth, I.; Arranz, S.; Casas, R.; Navarro, M.; Hervas, A.; Sisó, A.; et al. Effects of alcohol and polyphenols from beer on atherosclerotic biomarkers in high cardiovascular risk men: A randomized feeding trial. *Nutr. Metab. Cardiovasc. Dis.* 2015, 25, 36–45. [CrossRef] [PubMed]
- 3. De Gaetano, G.; Costanzo, S.; Di Castelnuovo, A.; Badimon, L.; Bejko, D.; Alkerwi, A.; Chiva-Blanch, G.; Estruch, R.; La Vecchia, C.; Panico, S.; et al. Effects of moderate beer consumption on health and disease: A consensus document. *Nutr. Metab. Cardiovasc. Dis.* 2016, 26, 443–467. [CrossRef] [PubMed]
- 4. Yang, D.; Gao, X. Research progress on the antioxidant biological activity of beer and strategy for applications. *Trends Food Sci. Technol.* **2021**, *110*, 754–764. [CrossRef]
- 5. Piazzon, A.; Forte, M.; Nardini, M. Characterization of phenolics content and antioxidant activity of different beer types. *J. Agric. Food. Chem.* **2010**, *58*, 10677–10683. [CrossRef] [PubMed]
- 6. Nardinia, M.; Garaguso, I. Characterization of bioactive compounds and antioxidant activity of fruit beers. *Food Chem.* **2020**, 305, 125437. [CrossRef]
- 7. Zapata, P.J.; Martínez-Esplá, A.; Gironés-Vilaplana, A.; Santos-Lax, D.; Noguera-Artiaga, L.; Carbonell-Barrachina, A.A. Phenolic, volatile, and sensory profiles of beer enriched by macerating quince fruits. *LWT Food Sci. Technol.* **2019**, *103*, 139–146. [CrossRef]

Sustainability **2024**, 16, 220

8. Kerpes, R.; Fischer, S.; Becker, T. The production of gluten-free beer: Degradation of hordeins during malting and brewing and the application of modern process technology focusing on endogenous malt peptidases. *Trends Food Sci. Technol.* **2017**, *67*, 129–138. [CrossRef]

- 9. Dragone, G.; Mussatto, S.I.; Almeida e Silva, J.B. High gravity brewing by continuous process using immobilised yeast: Effect of wort original gravity on fermentation performance. *J. Inst. Brew.* **2007**, *113*, 391–398. [CrossRef]
- 10. European Union. Regulation (EC) No 1333/2008 of the European Parliament and of the Council of 16 December 2008 on food additives. *Off. J. Eur. Union* **2008**, *354*, 16–33.
- 11. Yadav, R.; Yadav, N.; Saini, P.; Kaur, D.; Kumar, R. Potential Value Addition from Cereal and Pulse Processed By-Products: A Review. Sustain. Food Waste Manag. 2021, 9, 155–176. [CrossRef]
- 12. Rachwał, K.; Waśko, A.; Gustaw, K.; Polak-Berecka, M. Utilization of brewery wastes in food industry. *PeerJ* **2020**, 8, e9427. [CrossRef] [PubMed]
- 13. Hajji, T.; Mansouri, S.; Vecino-Bello, X.; Cruz-Freire, J.M.; Rezgui, S.; Ferchichi, A. Identification and characterization of phenolic compounds extracted from barley husks by LC-MS and antioxidant activity in vitro. *J. Cereal Sci.* **2018**, *81*, 83–90. [CrossRef]
- 14. Barbosa-Pereira, L.; Bilbao, A.; Vilches, P.; Angulo, I.; LLuis, J.; Fité, B.; Paseiro-Losada, P.; Cruz, J.M. Brewery waste as a potential source of phenolic compounds: Optimisation of the extraction process and evaluation of antioxidant and antimicrobial activities. *Food Chem.* **2014**, *145*, 191–197. [CrossRef] [PubMed]
- 15. Betancur, M.I.; Motoki, K.; Spence, C.; Velasco, C. Factors influencing the choice of beer: A review. *Food Res. Int.* **2020**, *137*, 109367. [CrossRef]
- 16. Bezerril, F.; Pimentel, C.T.; Peixoto de Aquino, K.; Schabo, D.C.; Heli Paiva Rodrigues, M.; dos Santos Lima, M.; Schaffner, D.W.; Furlong, E.B.; Magnani, M. Wheat craft beer made from AFB1-contaminated wheat malt contains detectable mycotoxins, retains quality attributes, but differs in some fermentation metabolites. *Food Res. Int.* 2023, 172, 112774. [CrossRef]
- 17. Panda, R.; Zoerb, H.F.; Cho, C.Y.; Jackson, L.S.; Garber, E.A.E. Detection and Quantification of Gluten during the Brewing and Fermentation of Beer Using Antibody-Based Technologies. *J. Food Prot.* **2015**, *78*, 1167–1177. [CrossRef]
- 18. Dabija, A. Biotechnologies in the Fermentative Food Industry; Oim Publishing House: Iasi, Romania, 2010.
- 19. Ezati, M.; Ghavamipour, F.; Adibi, H.; Pouraghajan, K.; Arab, S.S.; Sajedi, R.H.; Khodarahmi, R. Design, synthesis, spectroscopic characterizations, antidiabetic, *in silico* and kinetic evaluation of novel curcumin-fused aldohexoses. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2023, 285, 121806. [CrossRef]
- 20. Banu, C. Malt and Beer Technology; Technical Publishing House: Bucharest, Romania, 2003.
- 21. Berzescu, P. Beer and Malt Technology; Ceres Publishing House: Bucharest, Romania, 1981.
- 22. Pires, E.J.; Ruiz, H.A.; Teixeira, J.A.; Vicente, A.A. A new approach on brewer's spent grains treatment and potential use as lignocellulosic yeast cells carriers. *J. Agric. Food Chem.* **2012**, *60*, 5994–5999. [CrossRef]
- 23. Outeiriño, D.; Costa-Trigo, I.; Paz, A.; Deive, F.J.; Rodríguez, A.; Domínguez, J.M. Biorefining brewery spent grain polysaccharides through biotuning of ionic liquids. *Carbohydr. Polym.* **2019**, 203, 265–274. [CrossRef]
- 24. Qazanfarzadeh, Z.; Ganesan, A.R.; Mariniello, L.; Conterno, L.; Kumaravel, V. Valorization of brewer's spent grain for sustainable food packaging. *J. Clean. Prod.* **2023**, *385*, 135726. [CrossRef]
- 25. Bonato, S.V.; De Jesus Pacheco, D.A.; Schwengber ten Caten, C.; Caro, D. The missing link of circularity in small breweries' value chains: Unveiling strategies for waste management and biomass valorization. *J. Clean. Prod.* **2022**, *336*, 130275. [CrossRef]
- 26. Kerby, C.; Vriesekoop, F. An overview of the utilisation of brewery by-products as generated by British craft breweries. *Beverages* **2017**, *3*, 24. [CrossRef]
- 27. De Souza, L.; Zambom, M.; Alcalde, C.R.; Fernandes, T.; Castagnara, D.D.; Radis, A.C.; Santos, S.M.; Possamai, A.P.; Pasqualoto, M. Feed intake, nutrient digestibility, milk production and composition in dairy cows fed silage of wet brewers' grain. *Semin. Ciênc. Agrár.* 2016, 37, 1069–1080. [CrossRef]
- 28. Faccenda, A.; Zambom, M.; Castagnara, D.; de Avila, A.S.; Fernandes, T.; Eckstein, E.I.; Anschau, F.A.; Schneider, C.R. Use of dried brewers' grains instead of soybean meal to feed lactating cows. *Rev. Bras. Zootec.* **2017**, *46*, 39–46. [CrossRef]
- 29. Radzik-Rant, A.; Rant, W.; Niznikowski, R.; Swiatek, M.; Szymanska, Z.; Slezak, M.; Niemiec, T. The effect of the addition of wet brewers' grain to the diet of lambs on body weight gain, slaughter value and meat quality. *Arch. Anim. Breed.* **2018**, *61*, 245–251. [CrossRef]
- 30. Kim, H.; Hwang, K.; Song, D.; Lee, S.; Choi, M.; Lim, Y.; Choi, J.; Choi, Y.; Kim, H.; Kim, C. Effects of dietary fiber extracts from brewer's spent grain on quality characteristics of chicken patties cooked in convective oven. *J. Am. Soc. Brew. Chem.* **2013**, 33, 45–52. [CrossRef]
- 31. Choi, M.S.; Choi, Y.S.; Kim, H.W.; Hwang, K.E.; Song, D.H.; Lee, S.Y.; Kim, C.J.; Hwang, K.; Song, D.; Lee, S.; et al. Effects of replacing pork back fat with brewer's spent grain dietary fiber on quality characteristics of reduced-fat chicken sausages. *Food Sci. Anim. Resour.* **2014**, *34*, 158–165. [CrossRef]
- 32. Waters, D.M.; Jacob, F.; Titze, J.; Arendt, E.K.; Zannini, E. Fibre, protein and mineral fortification of wheat bread through milledand fermented brewer's spent grain enrichment. *Eur. Food Res. Technol.* **2012**, 235, 767–778. [CrossRef]
- 33. Xie, Y.; Bao, J.; Li, W.; Sun, Z.; Gao, R.; Wu, Z.; Yu, Z. Effects of Applying Lactic Acid Bacteria and Molasses on the Fermentation Quality, Protein Fractions and In Vitro Digestibility of Baled Alfalfa Silage. *Agronomy* **2021**, *11*, 91. [CrossRef]
- 34. Rodriguez, L.M.; Camina, J.L.; Borroni, V.; Perez, E.E. Protein recovery from brewery solid wastes. *Food Chem.* **2023**, 407, 134810. [CrossRef] [PubMed]

Sustainability **2024**, 16, 220

35. Singleton, V.L.; Rossi, J.A. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *Am. J. Enol. Vitic.* **1965**, *16*, 144–158. [CrossRef]

- 36. Vieira, E.F.; Carvalho, J.; Pinto, E.; Cunha, S.; Almeida, A.A.; Ferreira, I.M.P.L.V.O. Nutritive value, antioxidant activity and phenolic compounds profile of brewer's spent yeast extract. *J. Food Compos. Anal.* **2016**, *52*, 44–51. [CrossRef]
- 37. Viana, A.C.; Colombo Pimentel, T.; Borges do Vale, R.; Santos Clementino, L.; Ferreira, E.T.J.; Magnani, M.; dos Santos Lima, M. American pale Ale craft beer: Influence of brewer's yeast strains on the chemical composition and antioxidant capacity. *LWT Food Sci. Technol.* **2021**, *152*, 112317. [CrossRef]
- 38. Leitao, C.; Marchioni, E.; Bergaentzl, B.; Zhao, M.; Didierjean, L.; Taidi, B.; Ennahar, S. Effects of processing steps on the phenolic content and antioxidant activity of beer. *J. Agric. Food Chem.* **2011**, *59*, 1249–1255. [CrossRef] [PubMed]
- 39. Humia, B.V.; Santosa, K.S.; Kleveston Schneider, J.; Leal, I.L.; de Abreu Barreto, G.; Batista, T.; Souza Machado, B.A.; Druzian, J.I.; Krause, L.C.; da Costa Mendonça, M.; et al. Physicochemical and sensory profile of Beauregard sweet potato beer. *Food Chem.* **2020**, 312, 126087. [CrossRef]
- 40. Puligundla, P.; Mok, C.; Park, S. Advances in the valorization of spent brewer's yeast. *Innov. Food Sci. Emerg. Technol.* **2020**, 62, 102350. [CrossRef]
- 41. Guan, Y.; Xu, X.; Liu, C.; Wang, J.; Niu, C.; Zheng, F.; Li, Q. Evaluating the physiology and fermentation performance of the lager yeast during very high gravity brewing with increased temperature. *LWT Food Sci. Technol.* **2023**, *173*, 114312. [CrossRef]
- 42. Bachmann, A.A.L.; Calvete, T.; Feris, L.A. Potential applications of brewery spent grain: Critical overview. *J. Environ. Chem. Eng.* **2022**, *10*, 106951. [CrossRef]
- 43. Atalay, P.; Perendeci, N.A.; Goksungur, M.Y. Valorization of brewery waste. J. Eng. Sci. 2020, 26, 1257–1266. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.