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The Potential of Spent Barley as a Functional Food Ingredient: Study on the Comparison of Dietary Fiber and Bioactivity †

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Abstract: This research aimed to conduct a comparison of 8 different forms of brewery spent grain (BSG) on their polyphenolic content and antioxidant capacity as part of their potential as a functional food ingredient. The BSGs were dried until they reached a stable weight, grounded to pass through a 385 μm sieve and were vacuum packed in non-transparent packaging for further analysis. The results showed that BSG contained a high dietary fiber content which was dominated by a insoluble dietary fiber level of about 38.0–43.9% and a soluble dietary fiber content of about 3.9–9.6%. There were three groups of polyphenolic identified: flavan-3-ols, phenolic acids and flavonols at quantities of 362.1–1165.7 mg/kg, 65.8–122.5 mg/kg and 3.6–13.8 mg/kg, respectively. Antioxidant capacity was examined using an in vitro assessment: the 2,2′-Azinobis-(3-Ethylbenzthiazolin-6-Sulfonic Acid) (ABTS) capacity ranged from 0.086 to 0.241 mmol Trolox/100 g while the ferric reducing antioxidant potential (FRAP) capacity ranged from 0.106 to 0.306 μmol TE/100 g. In conclusion, BSG as a brewery waste can potentially be used as a functional food ingredient due to its properties. It is suggested that further studies are needed to explore BSG's impact on the development of functional food products.

Keywords: brewery spent grain; valorization; agricultural by-products; functional food; dietary fiber; polyphenolic compounds; antioxidant

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1. Introduction

Brewery spent grain (BSG), a by-product of the brewery industry, is generated using about 41% of beer waste production and 31% of malt materials [1,2]. A total of 20 kg of BSG is obtained from a 100 dm^3 beer load. Notably, in 2018, 1.94 billion hl of beer was produced worldwide [3]. Agro-industrial by-products are renewable resources because they are non-hazardous forms of waste. Valorization of biowaste is profitable for environmental, economic and human health reasons [4]. BSG has considerable potential to be used for several purposes such as for animal feed, food ingredients, polymer production, microbial products and nutritional applications [2]. The versatility of BSG is supported by its fiber compounds. Fiber is a good source of nutraceutical and nutrition, biopolymer and bioactive compounds such as phenolic compounds and substrates for microflora, as well as a source of bio-chemicals and biofuels [5,6].

There are some factors which affect the characteristics of BSG, including genetic variations of the crops used, the specificity of brewery production, treatment and pre-treatment after beer production [7]. Pre-treatment strategies, chemical and physical techniques have been studied involving BSG, specifically for its impact on protein quality [8]. In addition, the brewing process affected the amount of hydroxycinnamic acid in BSG [9], while drying methods [7] and types of malts [10] have been compared and showed that BSG has an impact on their polyphenolic and antioxidant capacity. Furthermore, different types of solvent used for polyphenolic extraction from BSG impacted the bioactivity of the compounds [11].

Those differences show that any treatments or methods directly impact the BSG's properties, which leads to the differences in the effects of BSG products. There is a lack of reliable scientific reports on comparison of the quality of BSGs from various sources. Thus, this study aimed to identify the differences of BSG from eight different brewery industries based on their polyphenolic content and antioxidant capacity.

2. Materials and Methods

2.1. Materials

BSGs were obtained from 8 different brewery industries in Poland (1 big brewery plant and 1 craft brewery), Germany (2 big and 2 small scale breweries) and Estonia, and were directly dried by convective drying. The samples were then ground using a mill laboratory scale to reach a maximum particle size of about 385 μm ± 10%. The samples were kept in aluminum bags and a chiller room for further analysis. All of the chemicals used were of analytical grades (Chempur, Wroclaw, Poland).

2.2. Chemical Composition and Bioactivity

Dietary fiber including non-soluble and total dietary fiber were assessed according to AOAC 991.43, while soluble dietary fiber was calculated by difference. Antioxidant capacities were studied in vitro in ferric reducing antioxidant potential (FRAP) and 2,2′-Azinobis-(3-Ethylbenzthiazolin-6-Sulfonic Acid) (ABTS) [12], while total polyphenolic was assessed using the UPLC-PDA-FL method [13]. The extraction method for total polyphenolic and antioxidant analysis was carried out by using ultrasound-assisted extraction (UAE).

3. Results

3.1. Dietary Fiber Composition

Total dietary fiber (TDF), soluble dietary fiber (SDF) and insoluble dietary fiber (IDF) are shown in Table 1. There is a variability shown for the fiber profile within the 8 BSG samples. The value for SDF were 3.98–9.66% while IDF and TDF were 36.37–43.97% and 43.97–53.56%, respectively.

3.2. Total Polyphenolic Content and Antioxidant Capacity

There are three major groups of polyphenolic compounds which were identified from BSG: flavonols, phenolic acids and flavan-3-ols and antioxidant capacity, which are shown in Table 2. Regarding their abundance, flavan-3-ols is the highest followed by phenolic acids and flavonols. The values for Flavan-3-ols were 362.119–1165.698 mg/kg dw while phenolic acids and flavonols were 65.768–122.532 mg/kg dw and 3.590–13.778 mg/kg dw, respectively. In general, the ability of BSG as an antioxidant is higher for FRAP except for BSG VIII. Antioxidant capacities for ABTS and FRAP were 0.086–0.241 mmol Trolox/100 g dw and 0.106–0.306 μmol TE/100 g dw for the samples, respectively.

4. Discussion

The SDF obtained on this study is higher and IDF is lower than in other studies, which reported 1.3% SDF and 58.2% IDF in BSG [14]. This result might be different due to the particle size of the spent grain, as it was noticed that the variability in particle size affects the fiber composition and amount [15]. However, the amount of TDF was in the range of other reports at 51–53% [16,17]. Reducing particle size of BSG transformed the IDF into SDF, thus the amount of IDF will increase and the amount of SDF decreases at the same time [15]. The SDF of BSG consisted of several monosaccharides such as rhamnose, arabinose, xylose, mannose, glucose and galactose in order of the retention time [18]. Moreover, BSG approximately contained 15–26% cellulose, 15–34% hemicellulose and 12–31% lignin [2,4,5,19–21].

Table 1. Dietary fiber composition of 8 different spent grains.

Spent Grain	Dietary Fiber (%)		
	Soluble	Insoluble	Total
I	3.980	41.525	45.505
II	6.040	43.095	49.135
III	9.724	37.651	47.375
IV	9.588	43.972	53.560
V	8.221	36.219	44.440
VI	5.959	38.015	43.975
VII	7.103	43.856	50.959
VIII	7.721	40.589	48.310

Note: I: Foundation II German Pale Ale; II: Bojanowo; III: WB; IV: Onnevalemi Komonendid; V: Drunken Soiler India Pale Ale, VI: Sto Mostow; VII: Fest; VIII: Elveliksiirid.

Table 2. Polyphenolic and antioxidant capacity of 8 different spent grains.

Spent Grain	Polyphenolic (mg/kg)				Antioxidant	
	Flavonols	Phenolic Acids	Flavan-3-ols	Total	ABTS	FRAP
I	10.06	100.55	824.95	935.56	0.086	0.106
II	13.78	96.10	886.41	996.29	0.091	0.155
III	12.69	122.53	1165.70	1300.92	0.154	0.253
IV	11.92	68.97	432.78	513.66	0.152	0.249
V	7.53	104.13	824.58	936.24	0.105	0.204
VI	13.56	108.24	527.07	648.86	0.184	0.306
VII	9.70	115.28	529.50	654.49	0.172	0.278
VIII	3.59	65.77	362.12	431.48	0.241	0.200

Note: *ABTS unit: mmol Trolox/100 g dw; FRAP unit: μmol TE/100 g dw; I: Foundation II German Pale Ale; II: Bojanowo; III: WB; IV: Onnevalemi Komonendid; V: Drunken Soiler India Pale Ale, VI: Sto Mostow; VII: Fest; VIII: Elveliksiirid.

The benefits of DF for human health have been widely known, especially for non-communicable diseases. It has some properties for human health such as regulating hypoglycemia, inhibiting a-amylase activity and binding cholesterol and sodium chelate [22]. DF is also able to regulate diarrhea by promoting defecation [23]. Noticeably, SDF from BSG increased activities and mRNA expression levels of antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT) and glutathione peroxidase (GPx) [18]. The ability of the DF properties might connect with polyphenolic content. Removing the polyphenolic bounds from DF could decrease the antioxidant capacity, as well as the prebiotic properties of the DF [24].

In this study, polyphenols compounds were identified in three different groups: flavonols, phenolic acids and flavan-3-ols. It was discovered that phenolic acids appeared with the most abundance compounds (Figure 1). Hydroxycinnamic acid (HA) is the most abundance phenolic acid from BSG [9]. The peaks detected in Figure 1 might be responsible for HA groups such as ferulic acid (FA), *p*-coumaric acid (*p*-CA) derivatives, FA derivatives, *p*-CA, caffeic acid (CA) and CA derivatives.

As was observed in other parameters, the amounts of polyphenolic compounds varied in between the 8 different samples. The differences in amount of phenolic compounds depend on the grain type, brewer process as well as environmental factors such as soil type, sun exposure and climate conditions during the plantation [9]. The higher the polyphenolic content the higher the FRAP antioxidant capacity, as well as the DNA protection induced by H_2O_2 [25]. Total flavonoids are related to DPPH capability of BSG regarding the simple regression analysis [21]. As was mentioned previously, fiber might be connected to the polyphenolic content due to the attachment of phenolic to fiber functional groups.

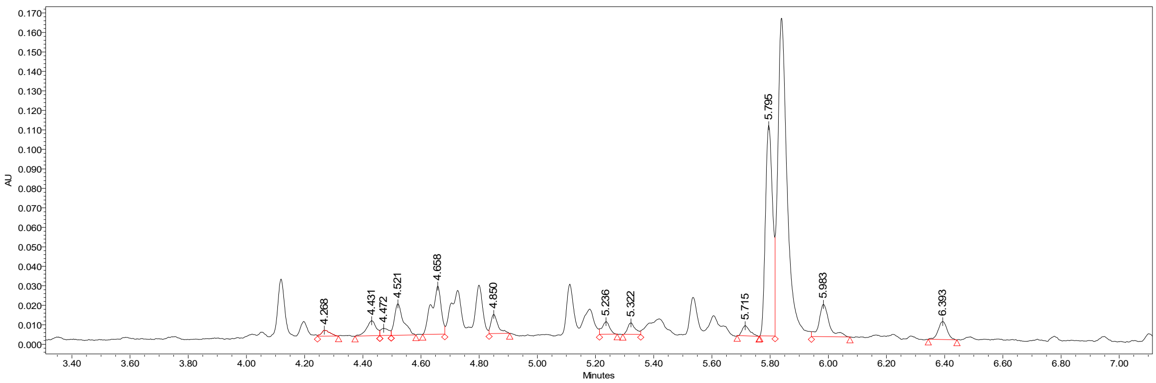

Figure 1. Chromatogram of phenolic acids of brewers spent grain.

The variability of antioxidant abilities (FRAP and DPPH) of BSG depended on extraction processes such as solvents and the methods used [6,21]. Surprisingly, the antioxidant capacity of BSG extract was higher compared to synthetic antioxidants and almost the same as the ability of BHA as an antioxidant [6]. In addition, the crude extract of BSG showed antimicrobial properties against both gram negative and gram positive bacteria. Polyphenolic compounds including protocatechuic, caffeic, *p*-coumaric, ferulic acid and catechin were responsible for the bioactivity of BSG. In this research, there was no evidence to show the relation between antioxidant capacity with other parameters studied such as dietary fiber and polyphenolic content.

5. Conclusions

In summary, BSG expresses beneficial properties as a functional food ingredient based on the dietary fiber composition, polyphenolic compounds and the antioxidant activity of the extract of BSG. However, it was observed that different brewery sources led to different BSG properties such as physical properties, chemical composition and biological activity. From this result, it is suggested that further study is needed to improve the BSG impact on the processing as well as final products of functional food.

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