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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 was aimed to study the comparison of 8 different brewer's spent grain (BSG) on their polyphenolic content and antioxidant capacity as their potential as functional food ingredient. The BSG were dried until they reached a stable weight, grounded to pass 385 µm sieve and they were vacuum packed in non-transparent packaging for further analysis. The result showed that BSG contained high dietary fiber content which was dominated by insoluble dietary fiber about 38.0–43.9% while soluble dietary fiber content about 3.9–9.6%. There were three groups of polyphenolic identified: flavan-3-ols, phenolic acids and flavonols about 362.1–1165.7 mg/kg, 65.8–122.5 mg/kg and 3.6–13.8 mg/kg, respectively. Antioxidant capacity were carried out in in vitro assessment: ABTS capacity was ranging from 0.086 to 0.241 mmol Trolox/100 g while FRAP capacity was from 0.106 to 0.306 µmol TE/100 g. In conclusion, BSG as a brewery waste is potentially to be used as a functional food ingredient for their properties. It is suggested that further studies are needed to explore their impact on the development of functional food products.

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

1. Introduction

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

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

Those differences depict that any treatments or methods directly impact the BSG properties which lead to the differences in the effects of approach products. There is a lack of reliable scientific report on comparison of the quality of BSG from various sources. Thus, this study is aimed to identify the differences of BSG from eight different brewery industries for their polyphenolic content and antioxidant capacity.

2. Materials and Methods

2.1. Materials

BSG 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, directly dried by convective drying. The samples were then ground using a mill laboratory scale to reach maximum particle size about 385 μm ± 10%. The samples were kept in aluminium bags and chiller room for further analysis. All 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) [13], meanwhile total polyphenolic was assessed using UPLC-PDA-FL method [14]. Extraction method for total polyphenolic and antioxidant analysis was carried out by ultrasound-assisted extraction (UAE).

3. Results

3.1. Dietary Fiber Composition

TDF, SDF and IDF are shown in Table 1. There is a variability within 8 BSG samples for fiber profile. SDF varied between 3.98–9.66% while IDF and TDF varied between 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, including 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. Flavan-3-ols varied from 362.119–1165.698 mg/kg dw while phenolic acids and flavonols were ranging between 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 ranging from 0.086–0.241 mmol Trolox/100 g dw and 0.106–0.306 μmol TE/100 g dw sample respectively.

4. Discussion

SDF obtained on this study is higher and IDF is lower than other study which reported a 1.3% of SDF and 58.2% of IDF in BSG [12]. This result might be different due to the particle size of the spent grain as it is noticed that the variability in particle size varies the fiber composition and amount [15]. However, the amount of TDF is in the range of other reports between 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 decrease in the same time [15]. SDF of BSG consisted of several monosaccharides such as rhamnose, arabinose, xylose, mannose, glucose, galactose in order of the retention time [18]. Moreover, BSG approximately contained cellulose 15–26%, hemicellulose (15–34%) and lignin (12–31%) [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 grain.

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 benefit of DF for human health has been widely known, especially in non-communicable diseases. It has some properties for human health such as regulating hypoglycemia, inhibiting a-amylase activity, 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 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 group such as ferulic acid (FA), *p*-coumaric acid (*p*-CA) derivatives, FA derivatives, *p*-CA, caffeic acid (CA) and CA derivatives.

As it 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 highest the polyphenolic content the highest the FRAP antioxidant capacity as well as the DNA protective induced by H_2O_2 [25]. Total flavonoids is related to DPPH capability of BSG regarding the simple regression analysis [21]. As it was mentioned previously, fiber might be connected to the polyphenolic content due to the attachment of phenolic to fiber functional groups.

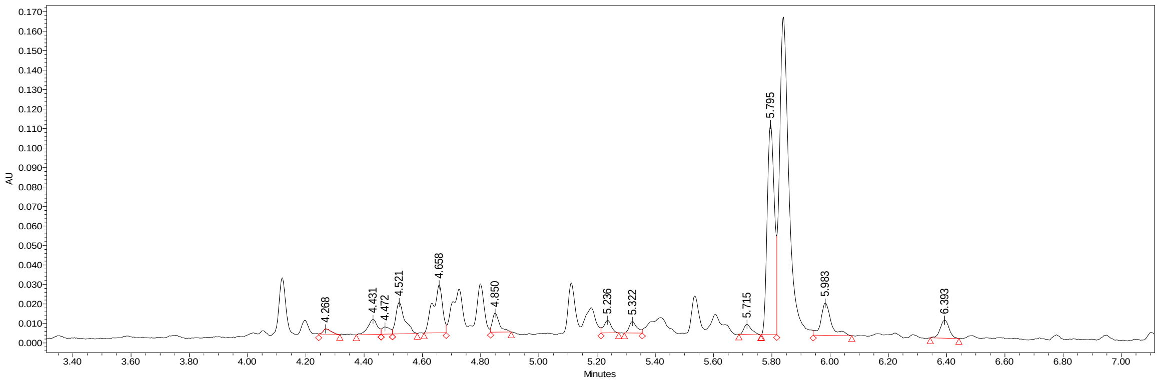

Figure 1. Chromatogram of phenolic acids of BSG.

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

5. Conclusions

Summing up, 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 source of brewery obtained different properties such as physical properties, chemical composition and biological activity. From this result, it is suggested that further study to improve the BSG impact on the processing as well as final products of functional food is needed.

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