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Original article

Chemical compositions, antioxidant activities and techno-functionality of spent grain treated by autoclave treatment: evaluation of water and temperature levels

Joncer Naibaho,[1]* Łukasz Bobak,[1] Anna Pudło,[1] Aneta Wojdyło,[2] Safira Noor Andayani,[3] Leonie Margaretha Widya Pangestika,[4] Małgorzata Korzeniowska[1]* & Baoru Yang[5]

1 Department of Functional Food Products Development, Faculty of Biotechnology and Food Science, Wroclaw University of Environmental and Life Sciences, Wroclaw 51-630, Poland
2 Department of Fruit, Vegetable and Plant Nutraceutical Technology, Faculty of Biotechnology and Food Science, Wrocław University of Environmental and Life Sciences, Wroclaw 51-630, Poland
3 Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Pendidikan Ganesha, Singaraja 81116, Indonesia
4 Faculty of Technobiology, Universitas Atma Jaya Yogyakarta, Yogyakarta 55281, Indonesia
5 Food Chemistry and Food Development, Department of Life Technologies, University of Turku, Turku 20014, Finland

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Summary Autoclave heating (AH) has been applied to modify the dietary fibre composition of dried brewers' spent grain (BSG) flour, which required multiple drying processes. The current study aimed to investigate the influence of the thermal levels and water ratio on AH, as an alternative, in altering the chemical compositions, antioxidant properties, and functionality of undried fresh BSG. The results showed that AH converted the saturated fatty acids into polyunsaturated fatty acids. AH reduced ketones and furans regardless of the water ratio while the amounts of aldehydes, alcohols, alkenes, and fatty acids depended on the water ratio. The elimination and formation of several volatile compounds were identified due to the AH depending on the water ratio. The total flavan-3-ols, antioxidant activities, and water-holding capacity of BSG were improved as an impact of thermal elevation and regardless of the water ratio. In conclusion, AH treatment on fresh, undried BSG showed a beneficial performance in improving the quality of BSG for further valorisation as a value-added by-product.

Keywords Agroindustrial by-products, fatty acids profile, oil-holding capacity, polyphenolic quantification, volatile compounds, water-holding capacity.

Introduction

Brewers' spent grain (BSG) has been reported for its nutritional value as well as biological properties due to the presence of polyphenolic compounds, protein, fatty acids, and dietary fibre (Lynch *et al.*, 2016; Naibaho & Korzeniowska, 2021a). The presence of polyphenolic compounds, protein, fatty acids, and dietary fibre is responsible for immunomodulatory properties as well as antimicrobial and anti-inflammatory activity. In addition to that, BSG possesses antioxidant activities such as lipid peroxidation, deoxyribose scavenging activity, superoxide dismutase, catalase, glutathione, DPPH, FRAP, and ABTS (Lynch *et al.*, 2016; Naibaho & Korzeniowska, 2021a). Although BSG possesses high potential as a food and nutraceutical ingredient, the majority of BSG still remains unused as land waste and a small fraction is used as animal/fish feed and fertiliser (Skendi *et al.*, 2018; Lao *et al.*, 2020). BSG is a complex material which is dominated by insoluble dietary fibre (Naibaho *et al.*, 2021). However, the biological properties of BSG are mostly studied due to the presence of phenolic compounds, followed by protein (Wen *et al.*, 2019; Naibaho *et al.*, 2022a, 2022b). Phenolic compounds exist in a hydroxyl group of dietary fibre while protein is entrapped in the vacuole cell wall of BSG materials, which consists of dietary fibre (Naibaho & Korzeniowska, 2021a). Besides the fact that BSG increased the nutritional value of BSG-added food products, BSG tended to inversely impact food processing aspects such as technological processing and mechanical properties which consequently diminished the physical appearance of the final products, as well as

*Correspondent: E-mails: joncer.naibaho@upwr.edu.pl (JN), malgorzata.korzeniowska@upwr.edu.pl (MK)

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sensory acceptability (Naibaho & Korzeniowska, 2021a).

Aiming to improve the yield of targeted compounds as well as its biological properties, several studies have also been conducted including solid-state fermentation (Cooray & Chen, 2018; Tan *et al*., 2019), pulsed electric field (Martín-García *et al*., 2020), pH elevation (Connolly *et al*., 2021), enzyme treatments (Connolly *et al*., 2019), and the combination of thermal and enzyme treatment (Budaraju *et al*., 2018). One of the most common physical treatments on BSG is thermal exposure such as steam explosion, microwave superheating, and autoclave treatment (Coelho *et al*., 2014; Kemppainen *et al*., 2016; Naibaho *et al*., 2021, 2022b). Temperature elevation improved the yield and enhanced the functionality of arabinoxylans and arabinoxylan-oligosaccharides as well as the availability of phenolic compounds (Budaraju *et al*., 2018). Furthermore, involvement of high pressure and temperature such as steam explosion, autoclave heating, high-pressure homogenisation, extrusion, and mechanical treatment improved the fibre functionality (Xie *et al*., 2017; Kieserling *et al*., 2019; Yan *et al*., 2019; Li *et al*., 2019a, 2019b). Furthermore, the addition of BSG in food products was limited due to its insoluble dietary fibre in disrupting the food matrix formation. Therefore, dietary fibre modification of BSG was emphasised (Naibaho & Korzeniowska, 2021a).

Autoclave heating treatment (AH) on rehydrated dried BSG was reported for its ability to degrade insoluble dietary fibre and convert it into soluble dietary fibre (Naibaho *et al*., 2021), thus improving the biological properties and polyphenolic composition (Naibaho *et al*., 2022b). Moreover, AH improved the functionality of dietary fibre from soybean curd residue (Li *et al*., 2019b), increased the resistant starch content in rice grains (Zheng *et al*., 2020), and enhanced the solubility-related properties and stability of the colloidal suspension (Nawaz *et al*., 2020). Usually, BSG is dried at a high temperature and/or stored at freeze temperature before it is used for certain treatments that require energy consumption. Treatment on fresh BSG is seemingly challenging due to its more practical use for several stakeholders and low-cost production. Treatment on wet or fresh BSG has been conducted in order to improve the protein and dietary fibre composition (He *et al*., 2019) (He *et al*., 2019). AH is a simple, easy-to-operate, and low-cost instrument; it is thus promising in BSG treatment, which involves high temperature and pressure elevation. AH has never been applied on wet BSG, particularly its impact on functionality, chemical constituents, and biological properties due to the different ratio of sludging. Most of the studied treatments were evaluated on phenolic compounds and/or protein composition in addition to dietary fibre composition. The influence of the energy input such as temperature and pressure on the fatty acid profile and volatile compounds of BSG has never been investigated. Volatile profile is an important parameter due to its direct impact on food product application, in terms of the valorisation of BSG as a food ingredient.

This study aimed to evaluate the influence of AH at different thermal exposures on undried fresh BSG properties including its functionality, polyphenolic composition, fatty acid profile, aromatic compounds, and *in vitro* antioxidant activities. Based on preexperiments, the addition of water in AH on BSG is technically needed to allow a homogenous thermal exposure. However, different amounts of water in fresh BSG generated different viscosities, thus impacting the mixing process and energy. Minimising water use in industries is suggested in order to achieve more sustainable treatments and implement cleaner processing methods (Bailone *et al*., 2022). Therefore, the current study investigated different levels of water addition into BSG slurry on AH. It was hypothesised that thermal decomposition of the BSG matrix directly altered the hydroxyl groups, which are polyphenolic compounds, as well as its antioxidant properties due to the degradation of dietary fibre. Previous studies investigated the influence of thermal degradation on protein extraction. However, degradation of the vacuole cell of BSG might release fatty acids, which has never been evaluated. Therefore, the current study evaluated the fatty acid composition of BSG in addition to volatile compounds as well as water-holding capacity and oil-holding capacity as a function of dietary fibre degradation.

Materials and methods

Materials

Fresh BSG with a moisture content of approximately 70–75% was supplied by a local brewery in Wroclaw, Poland. BSG was ground to pass 0.2 mm and kept in a polyethylene bag. BSG then was stored at a freezing temperature prior to the experiment.

UPLC-grade water was prepared by using the HLP SMART 1000s system (Hydrolab, Gdansk, Poland). Immediately, before use, the water was filtered using a 0.22 μm membrane filter. Trolox (6-hydro-2,5,7,8-tetramethylchroman-2-carboxylic acid) was purchased from Sigma-Aldrich (Steinheim, Germany). All the chemicals used were analytical grade.

Experimental design

BSG was allowed to defrost at room temperature just before the treatment. BSG was mixed properly with distilled water at two different ratios 1:1 and 1:2

(BSG:distilled water, *w*/*v*). Different time exposures on BSG by autoclave treatment identified that 12 min treatment generated a medium impact on the degradation of dietary fibre (Naibaho *et al.*, 2021), a higher impact on polyphenolic content at 90 °C, and a medium impact at 110 and 130 °C (Naibaho *et al.*, 2022b). Therefore, the current study was conducted at 12 min time exposures at different temperatures (90, 110, and 130 °C) and different water ratios. Untreated fresh BSG was provided for comparison. Therefore, seven samples were obtained. The BSG was then dried by oven drying at 75 °C for 16 h to reach a moisture below 6% (Table 1). The sample was ground using a lab scale blender for 5 min with a 10-s pause every 1 min. Samples were packed into aluminium foil and kept at 10 °C for further analysis.

The impact of the water ratio during the AH was evaluated on volatile compositions. The analysis performed only represented the water ratio, instead of the temperature level. The sample was chosen as the medium temperature treatment, which is 110 °C at two different ratios in comparison to the untreated BSG. Therefore, three different samples were compared for their volatile profiles.

Measurement of fatty acids composition by GC-MS

Total lipid was extracted following the procedures as described previously (Fărcaş *et al.*, 2015). Lipid was derivatised into fatty acid methyl esters (FAMEs) following procedures described in a previous study (Nowacki *et al.*, 2017). After that, the fatty acid profile was analysed by using a gas chromatograph (GC6890) coupled with a mass spectrometer 5983 MS (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a quadrupole mass detector. Separation was performed in a capillary column HP-88 (0.25 mm × 100 m) filled with an 88:12 cyanopropyl-aryl poly-siloxane bed with a grain size of 0.2 μm. Helium (flow rate 1 mL min^{-1}) was used as the mobile phase and the sample was injected in the split mode at 4:1. The program was set with an initial temperature of 60 °C for 2 min, heating at 20 °C min^{-1} to reach 180 °C and 3 °C min^{-1} to reach 220 °C. The temperature was held for 15 min. Heating continued to reach 250 °C at a rate of 5 °C min^{-1}, and the temperature was held for 8 min. The spectra were identified using the algorithm of searching the National Institute of Standards and Technology (NIST) library (2008 version).

Analysis of volatile compounds by GC–MS

Dried sample was mixed with distilled water at a ratio of 1:2 and closed properly. The volatiles were isolated by headspace solid-phase microextraction (HS-SPME) following procedures described in previous studies (Dong *et al.*, 2013; Ktenioudaki *et al.*, 2013; O'Shea *et al.*, 2017) by GC–MS 5975 C. The mixture was heated at 60 °C and the fibre (50/30 μm DVB/CAR/PDMS, Supelco) was exposed to the headspace for 30 min. The length of the fibre in the headspace was kept constant. The fibre was exposed to the injector of the gas chromatograph at 250 °C. The fibre was left at the port injector for 5 min to remove the contaminants. Helium was used as the carrier gas (1 mL min^{-1}). Separation of compounds was performed on a DB-5 column (30 m 0.25 mm, df = 0.25 lm, Agilent J&W, USA). The injector, ion source, and interface temperatures were set at 250, 200, and 260 °C, respectively. The mass spectrometer

Table 1 Fatty acids composition of autoclaved BSG

	BSG treatments						
Fatty acids (%)	**Control**	**90 °C/(1:1)**	**110 °C/(1:1)**	**130 °C/(1:1)**	**90 °C/(1:2)**	**110 °C/(1:2)**	**130 °C/(1:2)**
C15:0	–	–	–	29.28 ± 0.00	–	–	–
C16:0	40.22 ± 0.00	21.55 ± 0.00	21.63 ± 0.00	–	21.82 ± 0.00	21.38 ± 0.00	21.82 ± 0.00
C17:0	4.93 ± 0.00	–	–	–	–	–	–
C18:0	–	3.07 ± 0.00	2.67 ± 0.00	–	3.11 ± 0.00	3.07 ± 0.00	3.11 ± 0.00
C18:1 (n-9)	19.39 ± 0.00	17.96 ± 0.00	16.92 ± 0.00	–	17.40 ± 0.00	17.74 ± 0.00	17.40 ± 0.00
C18:2 (n-6)	32.81 ± 0.00	48.84 ± 0.00	51.67 ± 0.00	70.72 ± 0.00	48.92 ± 0.00	49.06 ± 0.00	48.92 ± 0.00
C18:3 (n-3)	2.66 ± 0.00	5.64 ± 0.00	5.40 ± 0.00	–	5.91 ± 0.00	5.90 ± 0.00	5.91 ± 0.00
C20	–	0.86 ± 0.00	–	–	0.83 ± 0.00	0.81 ± 0.00	0.83 ± 0.00
C20:1	–	2.09 ± 0.00	1.71 ± 0.00	–	2.01 ± 0.00	2.04 ± 0.00	2.01 ± 0.00
Total SFA	45.15 ± 0.00^{a}	25.47 ± 0.01^{e}	24.30 ± 0.00^{g}	29.28 ± 0.00^{b}	25.76 ± 0.00^{d}	25.26 ± 0.00^{f}	25.76 ± 0.00^{c}
Total MUFA	19.39 ± 0.00^{e}	20.05 ± 0.00^{a}	18.63 ± 0.00^{f}	0.00^{g}	19.41 ± 0.00^{d}	19.78 ± 0.00^{b}	19.41 ± 0.00^{c}
Total PUFA	35.46 ± 0.00^{g}	54.48 ± 0.00^{e}	57.07 ± 0.00^{b}	70.72 ± 0.00^{a}	54.83 ± 0.00^{d}	54.96 ± 0.00^{c}	54.83 ± 0.00^{f}

The data are shown as mean ± standard deviation with at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($P < 0.05$).

was operated in the electron-impact mode with the electron energy set at 70 eV and scan range of 40–400 m/z. The oven temperature was elevated from 40 to 250 C at a rate of 4 °C min^{-1}, and the temperature was held constant for 5 min. The peak area was measured either by full scanning or by choosing specific fragments. The volatile compounds were tentatively identified using the spectra of reference compounds from NIST.

Identification of polyphenolic by UPLC–MS/MS and *in vitro* antioxidant activities

Methanol extracts of BSG were prepared following the procedures as described previously (Turkiewicz *et al*., 2020b) with duplicates. *In vitro* antioxidant capabilities for ABTS and FRAP (Benzie & Strain, 1996; Re *et al*., 1999) in triplicate for duplicate extracts. The identification and quantification of flavan-3-ols and phenolic acids were performed by liquid chromatography–tandem mass spectrometry (LC–MS-MS) following procedures as described in the previous studies (Turkiewicz *et al*., 2020a, 2021; Tkacz *et al*., 2021). The assessment was performed in duplicate.

Analysis of techno-functional properties

The water-holding capacity (WHC) and oil-holding capacity (OHC) were performed to represent the techno-functionality of BSG following the procedures as described in a previous study (Ktenioudaki *et al*., 2013).

Statistical analysis

Statistical analysis was conducted using one-way analysis of variance (ANOVA) followed by Tukey's *post hoc* test in Statistica software version 13.5.0.17.

Results and discussion

Influence of AH on fatty acid compositions

The fatty acid composition of BSG is presented in Table 1. In general, the AH treatment reduced the amount of saturated fatty acids (SFA) and increased the level of polyunsaturated fatty acids (PUFA). The majority of AH improved the amount of monounsaturated fatty acids (MUFA) except on the ratio of 1:1 at 110 and 130 °C. The study revealed that AH decreased C17:0 at all temperatures and ratios. However, the formation of C15:0 was identified at 130 °C (1:1), C18:0 and C20:1 were observed in all treatments except at 130 °C (1:1), and C20:0 was observed at a 1:2 ratio and at 90 °C (1:1). Remarkably, the treatment at 130 °C (1:1) discharged the majority of fatty acid compared to that in untreated BSG. The results demonstrated that untreated BSG is dominated by C16:0, which is SFA; meanwhile, AH-treated BSG is dominated by C18:2 (n-6). However, in total, both treated and untreated BSG is dominated by PUFA. This result is aligned with the previous reports which identified that fatty acid of BSG is dominated by PUFA (Fărcaş *et al*., 2015; Balogun *et al*., 2017; Mallen & Najdanovic-Visak, 2018).

The results showed that AH allowed the rearrangement and/or depolymerisation of SFA into UFA. The modification of SFA into UFA in the current study also might be due to the release of UFA from the polysaccharides main chain due to the thermal exposure as observed previously (Rahman *et al*., 2021). It has been reported previously that higher temperatures increased the amount of UFA and reduced the amount of SFA (Mallen & Najdanovic-Visak, 2018) due to the increasing transesterification rate, which consequently improved the mass transfer from the matrix (Mallen & Najdanovic-Visak, 2018). It is widely accepted that PUFA benefits human health while SFA is recognised to induce non-communicable diseases. Therefore, AH on BSG improves the potential application of BSG in nutraceutical and/or functional food.

Impact of AH on the profile of volatile compounds

The impact of AH on volatile compounds of BSG was investigated in one of each ratio group (1:1 and 1:2) at the medium temperature (110 °C), and the result is presented in Table 2. In general, quantitative volatile compounds on BSG are dominated by the aldehydes group. The result showed that AH reduced the amount of ketones, alcohols, and furans and increased the levels of fatty acids and aldehydes. Furthermore, besides the alteration of quantitative amounts of volatile compounds, AT on BSG with different water ratios discharged and formed several volatile compounds on BSG.

AH with a water ratio at 1:2 increased the amount of aldehydes significantly ($P < 0.05$), while a ratio of 1:1 generated the same level as in the control. AH eliminated (E)-2-hexenal regardless of the water ratio, while it presented in untreated BSG. (E)-2-hexenal has been observed as a green leaf volatile, which has antifungal properties and is responsible for an unpleasant odour which deters fungi and insects (Kunishima *et al*., 2016). This compound might be present in BSG due to the application of pesticides during the plantation and/or storage of the grain prior to the brewing process. The present study demonstrated that AH is able to remove (E)-2-hexenal as a sign of chemical residue during the handling of grain. AH with a lower amount of water addition (1:1) removed (Z)-2-heptenal from BSG, while it was identified in untreated and 1:2

Table 2 Volatile compounds (%) of autoclave heating treated BSG (percentage of peak area)

Compounds	Treatments		
	Control	110 °C/(1:1)	110 °C/(1:2)
Aldehydes			
Butanal, 3-methyl-	4.48 ± 0.01	4.29 ± 0.23	4.23 ± 0.08
Pentanal	1.19 ± 0.01	1.33 ± 0.01	2.39 ± 0.03
Hexanal	17.30 ± 0.08	11.91 ± 0.06	16.18 ± 0.10
2-Hexenal, (E)-	0.55 ± 0.00	–	–
Heptanal	1.26 ± 0.01	1.62 ± 0.02	1.24 ± 0.06
2-Heptenal, (Z)-	1.13 ± 0.01	–	0.55 ± 0.03
2,4-Heptadienal, (E,E)-	0.53 ± 0.01	0.31 ± 0.03	0.22 ± 0.01
Octanal	–	1.34 ± 0.01	1.92 ± 0.07
2-Octenal, (E)-	3.63 ± 0.01	1.79 ± 0.11	2.42 ± 0.04
Nonanal	11.13 ± 0.15	6.17 ± 0.07	10.68 ± 0.06
2-Nonenal, (E)-	3.06 ± 0.01	0.99 ± 0.04	2.04 ± 0.02
2,4-Nonadienal, (E,E)-	0.88 ± 0.01	0.51 ± 0.02	0.49 ± 0.03
Decanal	1.92 ± 0.02	1.58 ± 0.04	1.74 ± 0.00
Dodecanal	–	0.21 ± 0.01	–
2,4-Dodecadienal, (E,E)-	–	–	0.36 ± 0.01
2,4-Decadienal, (E,E)-	–	2.75 ± 0.05	1.97 ± 0.07
Undecanal	0.36 ± 0.00	0.20 ± 0.01	–
Benzaldehyde	4.93 ± 0.03	5.57 ± 0.07	2.38 ± 0.02
Benzeneacetaldehyde	7.11 ± 0.09	4.47 ± 0.00	4.27 ± 0.07
Ketones			
2-Hexanone, 5-methyl-	–	–	0.51 ± 0.01
2-Heptanone	1.24 ± 0.05	1.30 ± 0.02	0.62 ± 0.01
5-Hepten-2-one, 6-methyl-	0.61 ± 0.05	0.38 ± 0.02	0.21 ± 0.01
3-Octen-2-one, (E)-	1.96 ± 0.14	0.70 ± 0.01	–
3,5-Octadien-2-one, (E,E)-	7.52 ± 0.47	3.41 ± 0.04	4.72 ± 0.05
5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	0.44 ± 0.02	0.48 ± 0.01	–
2(3H)-Furanone, 5-heptyldihydro-	0.62 ± 0.02	0.43 ± 0.02	0.22 ± 0.01
Alcohols			
Ethanol, 2-phenoxy-	–	0.32 ± 0.01	0.55 ± 0.01
2,4-Hexadien-1-ol	–	–	0.56 ± 0.03
2-Hexyn-1-ol	–	–	0.49 ± 0.01
1-Octen-3-ol	1.80 ± 0.14	1.57 ± 0.02	0.59 ± 0.03
2-Octen-1-ol, (Z)-	0.43 ± 0.02	–	0.22 ± 0.01
3,5-Octadien-2-ol	–	–	0.51 ± 0.03
Nona-3,5-dien-2-ol	0.56 ± 0.02	–	–
Hept-2-en-1-ol	0.39 ± 0.01	–	–
4,4,6-Trimethyl-cyclohex-2-en-1-ol	1.10 ± 0.06	0.29 ± 0.00	–
2-Butyl-2,7-octadien-1-ol	0.57 ± 0.04	–	–
1-Tetradecanol	0.38 ± 0.03	0.23 ± 0.00	–
1-Hexadecanol	1.11 ± 0.09	1.66 ± 0.02	–
2-Methoxy-4-vinylphenol	–	0.18 ± 0.00	–
Furans			
Furan, 2-pentyl-	7.60 ± 0.46	6.85 ± 0.08	6.07 ± 0.01
Furfural	–	0.31 ± 0.02	0.90 ± 0.03
Alkane			
Tridecane	4.72 ± 0.05	5.72 ± 0.07	4.18 ± 0.02
1-Tridecene	–	0.36 ± 0.02	–
Tetradecane, 2,6,10-trimethyl-	1.98 ± 0.04	0.45 ± 0.03	0.21 ± 0.00
Tetradecane	1.12 ± 0.05	1.23 ± 0.01	0.81 ± 0.03
1-Pentadecene	–	1.38 ± 0.01	0.73 ± 0.01
3-Heptadecene, (Z)-	–	0.19 ± 0.01	–
Nonadecane	0.41 ± 0.01	0.45 ± 0.02	–
Dodecane	3.39 ± 0.09	3.66 ± 0.02	3.37 ± 0.01
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	–	0.40 ± 0.02	–
Undecane	–	0.25 ± 0.00	0.46 ± 0.01
Fatty acids			
Acetic acid, cyano-	–	–	0.88 ± 0.01
Hexanoic acid	0.95 ± 0.05	1.09 ± 0.01	–
Hexanoic acid, 1-cyclopentylethyl ester	–	0.18 ± 0.01	–
n-hexadecanoic acid	–	–	1.18 ± 0.06
Other			
D-Limonene	1.61 ± 0.09	2.17 ± 0.03	1.53 ± 0.01
Benzene, 1-methyl-3-(1-methylethyl)-	–	0.52 ± 0.01	0.38 ± 0.02
Benzene, 1,3-bis (1,1-dimethylethyl)-	–	–	0.24 ± 0.01
1R-α-Pinene	–	0.72 ± 0.01	0.65 ± 0.01
Total			
Aldehydes	59.47 ± 0.07^{b}	63.14 ± 0.23^{ab}	69.24 ± 0.22^{a}
Ketones	12.39 ± 0.63^{a}	6.7 ± 0.01^{b}	6.27 ± 0.07^{b}
Alcohols	6.35 ± 0.11^{a}	4.24 ± 0.04^{b}	2.91 ± 0.08^{c}
Furans	7.60 ± 0.46^{a}	7.17 ± 0.08^{b}	6.97 ± 0.01^{b}
Alkene	11.62 ± 0.02^{b}	14.06 ± 0.01^{a}	9.75 ± 0.07^{c}
Fatty acid	0.95 ± 0.05^{c}	1.28 ± 0.04^{b}	2.06 ± 0.05^{a}
Others	1.61 ± 0.16^{c}	3.41 ± 0.05^{a}	2.79 ± 0.08^{b}

The data are shown as mean ± standard deviation with at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($P < 0.05$).

ratio treated BSG. (Z)-2-heptenal represents green and pungent odour perception in BSG (Dong *et al.*, 2013; Ktenioudaki *et al.*, 2013; Fărcaş *et al.*, 2015). This demonstrated that a lower amount of water (1:1) eliminated the unpleasant odour perception of BSG. AH with a higher water amount (1:2) destroyed the presence of undecanal, while it presented in untreated and 1:1 ratio treated BSG. Undecanal has never been reported on BSG; however, 2-undecenal has been reported in cells immobilised by BSG (Mallouchos *et al.*, 2007) and undecane was observed in grain (Buśko *et al.*, 2010). Undecanal is formed by the hydroformylation of decene (Kohlpaintner *et al.*, 2013). It has a pleasant odour, which is often found in perfumes (Kohlpaintner *et al.*, 2013). In other words, higher amounts of water (1:2) eliminated the pleasant odour of BSG.

The formation of octanal and (E,E)-2,4-decadienal in BSG was identified due to AH at both levels of

water addition. Dodecanal was formed at a lower water ratio (1:1) and (E,E)-2,4-dodecadienal was formed with a higher water addition (1:2). Octanal, (E, E)-2,4-decadienal, dodecanal, and (E,E)-2,4-dodecadienal has never been identified in BSG. However, octanal is present in barley and malt (Fărcaş *et al*., 2015), demonstrating fat, soap, lemon, and green odour perception (Dong *et al*., 2013). AH may have reformed the octanal as in its original form. (E, E)-2,4-decadienal was present in bread prepared with dried distilled grain, which was responsible for its rancid odour (Roth *et al*., 2016). This formation might be due to the high thermal exposure in the current study. (E,E)-2,4-decadienal has an odour activity value at 23.4% (Roth *et al*., 2016), which is much higher than the observed amount in the current study (maximum 3.34%). The influence of AH on the formation of rancid compounds ((E,E)-2,4-decadienal) can be ignored as the amount is much lower than the odour activity value. Dodecanal may be synthesised from dodecanol by dehydrogenation (Kohlpaintner *et al*., 2013), which demonstrated citrus oil odour perception; (E,E)-2,4-dodecadienal was identified in virgin olive oil (Giuffrè *et al*., 2020).

AH significantly ($P < 0.05$) reduced the amount of ketones to the same level at which both water level additions had no significant ($P > 0.05$) difference to each other. The addition of water on AH treatment eliminated 2-methyl-3-octanone. Furthermore, higher levels of water addition induced the formation of 5-methyl-2-hexanone and removed (E)-3-octen-2-one and (E)-6,10-dimethyl-5,9-undecadien-2-one. Those compounds have never been reported in BSG. 2-methyl-3-octanone was reported in processed meat products (Xia *et al*., 2020), which might be responsible for its meat-like odour perception; 5-methyl-2-hexanone was identified in black tea (Yan *et al*., 2022); (E)-3-octen-2-one is an aliphatic ketone, which was identified in pea protein isolate (Xu *et al*., 2020) and might represent rose, green and nut odour perception; (E)-6,10-dimethyl-5,9-undecadien-2-one or geranylacetone was observed as a flavour compound in mango (Pino *et al*., 2005). These results might demonstrate the ability of AH in eliminating meat-related odour perception and forming a green and fruity smell.

AH significantly reduced the amount of volatile alcohol in BSG. Regardless of the water level, AH eliminated nona-3,5-dien-2-ol, hept-2-en-1-ol, and 2-butyl-2,7-octadien-1-ol and induced the formation of 2-phenoxy-ethanol. All these eliminated alcohols were responsible for the essential oil flavour, as has been reported previously (Bannour *et al*., 2016; Vasanthakumar *et al*., 2019; Hota *et al*., 2022). However, 2-phenoxy-ethanol, as a new formed compound, has been observed in cereal grain (Buśko *et al*., 2010). Lower water addition (1:1) discharged (Z)-2-octen-1-ol and formed 2-methoxy-4-vinylphenol, which are responsible for a vinegar smell and flavouring agent compounds, respectively (Jeong *et al*., 2011; Le *et al*., 2012), while higher water addition (1:2) discharged 1-tetradecanol, 1-hexadecanol, and 4,4,6-trimethyl-cyclohex-2-en-1-ol and induced the formation of 2,4-hexadien-1-ol, 2-hexyn-1-ol, and 3,5-octadien-2-ol. The eliminated compounds are responsible for a fatty odour while the formed compounds are responsible for fruity and herbal perception (Noweck & Grafahrend, 2006; Feng *et al*., 2015; Wang *et al*., 2015; El-Tantawy *et al*., 2016; Polat *et al*., 2018; Ju *et al*., 2021). The results revealed that AH potentially removed the essential oil odour perception and dominantly formed pleasant smells including a grainy and desired flavour.

AH with a lower water addition formed several alkane compounds such as 1-tridecene, Z-3-heptadecene, and 3-ethyl-5-(2-ethylbutyl)-octadecane, in addition to 1-pentadecene and undecane, which were also formed at a higher water addition. All those formed compounds were identified as responsible for odour perception from medicinal plant extracts (Wang *et al*., 2015; Borgohain *et al*., 2022). In untreated BSG, only hexanoic acid was identified as a fatty acid, while AH (1:1) formed hexanoic acid and hexanoic acid 1-cyclopentyl-ethyl ester. AH (1:2) eliminated hexanoic acid and formed cyano-acetic acid and n-hexadecanoic acid. Furthermore, AH induced the formation of 1-methyl-3-(1-methylethyl)-benzene, 1R-α-pinene, and furfural. 1-methyl-3-(1-methylethyl)-benzene and 1R-α-pinene were identified in ginger (Ding *et al*., 2012), while furfural was reported due to the Maillard reaction in BSG-added bread (Ktenioudaki *et al*., 2013).

Seeing the significant modification in the profile of volatile compounds in BSG due to AH treatment, further investigation with the electronic nose is important. The identification of key odour compounds is suggested for further investigation to strengthen the findings in the current study.

Tentative quantification of polyphenolic compounds

The polyphenolic composition of BSG is presented in Table 3. The results revealed that the water ratio had no significant ($P > 0.05$) influence on the total flavan-3-ols and total polyphenolic composition. The higher the temperature, the higher the amount of flavan-3-ols and total polyphenol content, although 90 °C exposure led to the same level as that in control. A different pattern on the total phenolic acids was observed. The majority of the treatments increased the amount of total phenolic acids significantly to a certain level at which there was no significant difference among the treatments. These results suggested that AH at 110

Table 3 Physico-chemical and biological properties of autoclave heating treated BSG

Treatments	MC (%)	Fat (%)	WHC (g/g)	OHC (g/g)	ABTS (mmol Trolox per 100 g)	FRAP (mmol Trolox per 100 g)	Total flavan-3ols (mg kg^{-1})	Total phenolic acids (mg kg^{-1})	Total polyphenolic compounds (mg kg^{-1})
Control	5.39 ± 0.35^{a}	6.62 ± 0.31^{a}	2.90 ± 0.05^{d}	2.05 ± 0.01^{c}	0.11 ± 0.01^{c}	0.07 ± 0.01^{c}	122.79 ± 0.71^{c}	44.29 ± 2.12^{c}	167.07 ± 1.41^{d}
90 °C/(1:1)	4.79 ± 0.13^{a}	7.02 ± 0.23^{a}	3.47 ± 0.05^{bc}	2.02 ± 0.00^{e}	0.09 ± 0.02^{c}	0.05 ± 0.00^{c}	256.82 ± 15.02^{c}	69.38 ± 1.72^{c}	326.19 ± 0.85^{d}
110 °C/(1:1)	5.21 ± 0.01^{a}	8.52 ± 0.13^{a}	4.04 ± 0.01^{a}	2.07 ± 0.00^{b}	0.25 ± 0.00^{b}	0.20 ± 0.01^{b}	618.16 ± 23.42^{b}	130.41 ± 9.86^{ab}	748.56 ± 47.42^{bc}
130 °C/(1:1)	4.94 ± 0.01^{a}	9.23 ± 0.41^{a}	3.80 ± 0.03^{abc}	2.04 ± 0.00^{d}	0.33 ± 0.00^{a}	0.28 ± 0.02^{a}	996.62 ± 47.83^{a}	166.76 ± 1.35^{a}	1163.38 ± 49.18^{a}
90 °C/(1:2)	5.03 ± 0.14^{a}	6.70 ± 0.39^{a}	3.26 ± 0.07^{cd}	2.03 ± 0.00^{de}	0.09 ± 0.00^{c}	0.07 ± 0.00^{c}	216.64 ± 9.30^{c}	118.24 ± 7.15^{b}	334.89 ± 2.15^{d}
110 °C/(1:2)	5.11 ± 0.09^{a}	7.89 ± 0.11^{a}	3.88 ± 0.06^{ab}	2.05 ± 0.00^{c}	0.27 ± 0.00^{b}	0.23 ± 0.01^{b}	572.23 ± 29.73^{b}	70.18 ± 2.25^{c}	642.41 ± 31.99^{c}
130 °C/(1:2)	5.35 ± 0.05^{a}	8.51 ± 0.33^{a}	4.06 ± 0.04^{a}	2.10 ± 0.00^{a}	0.32 ± 0.02^{a}	0.29 ± 0.02^{a}	747.15 ± 5.79^{b}	128.83 ± 4.98^{ab}	875.98 ± 10.77^{b}

The data are shown as mean ± standard deviation with at least duplicate analysis. Letters show the significant differences from other treatment in the same column ($P < 0.05$).

and 130 °C is capable of increasing the release of flavan-3-ols and thus total polyphenols content up to 5–8-fold and 4–7-fold, respectively. This phenomenon might be due to the degradation of dietary fibre and/or vacuole cell disruption of BSG matrix.

The impact of thermal exposure on dried, untreated BSG by autoclave has been reported previously (Naibaho *et al.*, 2021), reporting that AH transformed the insoluble dietary fibre into a soluble one. This transformation might be aligned with the increase in flavan-3-ols and total polyphenols in the current study. Thermal exposure has been identified for disrupting the cell vacuoles and/or cleaving the covalent bonds (Rahman *et al.*, 2021), thus allowing the modification of lignin solubility (Ohra-aho *et al.*, 2016). As a consequence, it might lead to the release of certain functional groups including flavan-3-ols and total polyphenols. The improvement of phenolic acid in BSG has been identified due to the pulsed electric field treatment and thermal exposure (Budaraju *et al.*, 2018; Martín-García *et al.*, 2020), which intensified up to 1.7–2.7-fold (Martín-García *et al.*, 2020). The increase in the quantitative compounds in the current study due to the thermal exposure might be concomitant to the formation of certain compounds, as has been identified previously. Caffeic acid was absent at a lower temperature (<100 °C) but present at a higher temperature, while the presence of sinapic acid was observed at 160 °C oven heating (Rahman *et al.*, 2021).

AH at 90 °C generated the same level of polyphenols content as in the control due to its inefficiency in rupturing the crosslinking bond between polysaccharides and phenolic compounds (Sibhatu *et al.*, 2021). Meanwhile, high temperature is able to discharge ester-linked ferulic acid from polysaccharides functional groups, as reported previously (Sibhatu *et al.*, 2021). The results demonstrated that the crosslink between polysaccharides and phenolic acids seems to be more stable compared to that in flavan-3-ols. Different levels of temperatures generated almost the same amount of phenolic acids, although it is remarkably higher than untreated BSG. Of note is that none of the treatments reduced the polyphenolic compounds. A decline in phenolic acids by 4–6-times lower occurred due to the extraction methods (Bonifácio-Lopes *et al.*, 2020).

In vitro antioxidant capabilities

The results demonstrated that, the higher the thermal levels, the higher the increase in antioxidant activities of both FRAP and ABTS, regardless of the water ratio. However, AH at 90 °C had the same level as that in untreated BSG. This phenomenon might be aligned with the trend in the amount of flavan-3-ols, as mentioned in the previous section. Thermal

exposures at 110 and 130 °C released a higher amount of flavan-3-ols, thus enhancing the FRAP and ABTS properties of methanolic extracts from AH-treated BSG. ABTS defines the capability of the extracts in reducing the molecular oxygen and hydrogen peroxide (Benzie & Strain, 1996), and FRAP demonstrates the ability of the extracts in alleviating lipid oxidation (Rahman *et al*., 2021). By this, the current study revealed the ability of AH in improving the ability of BSG as a healthy ingredient, both as functional food and nutraceutical ingredient.

According to the previous studies, other compounds in BSG which play an important role in antioxidant capabilities of BSG include fatty acids such as palmitic, linoleic, oleic, and stearic acid (Fărcaş *et al*., 2015; Parekh *et al*., 2017; Tan *et al*., 2019). This might be slightly related to the fat content in the current study, although statistical significance was not observed. However, notably, the fat content was observed to be higher as the temperature was raised. Furthermore, as was mentioned in Influence of AH on fatty acid compositions Section, AH reduced the amount of SFA and concomitantly improved the amount of PUFA. This phenomenon might suggest an indirect link to the increase in the antioxidant activity, as discovered in this section. The improvement in antioxidant activity has also been observed previously (Budaraju *et al*., 2018). It was emphasised that the improvement in antioxidant activity had no correlation with the amount of bound phenolic compounds (Budaraju *et al*., 2018). Therefore, the improvement of antioxidant activity in the current study might be a result of free phenolic compounds. Furthermore, coumaric acid had a crucial impact on antioxidant properties of BSG (McCarthy *et al*., 2013). The specific phenolic compounds were not investigated in the current study. However, this might suggest that the antioxidant activity observed in the current study might only be due to certain compounds, which is seemingly important to investigate in the near future. Hydroxycinnamic acid is the most abundant phenolic acid from BSG including ferulic acid (FA), p-coumaric acid (p-CA) derivatives, FA derivatives, p-CA, caffeic acid (CA), and CA derivatives (McCarthy *et al*., 2013).

Impact of AH on the techno-functionality of BSG

The results showed that AH significantly ($P < 0.05$) enhanced WHC regardless of the water ratio. Statistically, the highest WHC was given by the higher temperature in both water ratios, while the lowest WHC was obtained in untreated BSG. This result demonstrated that AH improved the WHC of BSG as a sole impact of the temperature levels. The treated BSG had a range of 3.3–4.1 g/g WHC, while untreated BSG obtained WHC at 2.9 g/g. This number is aligned with the previous studies which reported that the WHC of BSG ranged from 2.9 to 4.3 g/g (Naibaho *et al*., 2021; Naibaho & Korzeniowska, 2021b). AH on dried BSG was observed to decrease the WHC of BSG (Naibaho *et al*., 2021), while the current study, which increased the WHC, was conducted on undried fresh BSG. In contrast, the majority of AH treatment decreased the OHC level of BSG. OHC in the current study appeared at the same range as previously reported, at a range of 1.9–2.2 g/g (Naibaho & Korzeniowska, 2021b). However, AH on dried BSG reduced the OHC level (Naibaho *et al*., 2021). Therefore, AH treatment on fresh BSG slurry benefits the techno-functionality of BSG. The ability of BSG in binding water is influenced by the presence of arabinoxylans (Steiner *et al*., 2015). By this, AH might have modified the polysaccharides composition of BSG, as mentioned earlier, in addition to the arabinoxylans profile. Techno-functional properties can be altered due to energy exposures. A reduction in WHC and OHC was observed due to the particle size reduction, while an increase was obtained as an impact of high-pressure treatment (Yan *et al*., 2019). The fluctuation of WHC and OHC was emphasised due to the exposure of hydrophilic groups as an impact of losing the dietary fibre structure (Yan *et al*., 2019). Improving the WHC benefits the texture and viscosity of food products (Benitez *et al*., 2019; Kieserling *et al*., 2019). Therefore, AH showed a beneficial performance in improving food structure formation.

Conclusion

The results revealed that AH is capable of reducing SFA, increasing PUFA and slightly altering the amount of MUFA. Quantitatively, AH reduced the amount of ketones, alcohols, and furans, while it intensified the aldehydes and volatile fatty acids, regardless of the water ratio. The alteration of the volatile compound profile was followed by the elimination and formation of several volatile compounds in BSG matrix depending on the water ratio. Furthermore, AH enriched the amount of total flavan-3-ols and, thus, the total polyphenolic compounds, and enhanced the antioxidant activities (ABTS and FRAP) and improved the WHC of BSG as an impact of thermal elevation and regardless of the water ratio. The study demonstrated that AH improved the quality of BSG as a functional food and nutraceutical ingredient from the perspective of bioactivity and functionality. Further investigation on polysaccharides composition, protein and amino acids profile as well as free fatty acids and storage stability related is seemingly important in order to understand the mechanisms and efficiency of AH in disrupting BSG matrix.

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Author contributions

Joncer Naibaho: Conceptualization (lead); data curation (lead); formal analysis (lead); funding acquisition (equal); methodology (equal); project administration (supporting); resources (supporting); software (lead); visualization (supporting); writing – original draft (lead); writing – review and editing (lead). **Łukasz Bobak:** Data curation (supporting); formal analysis (supporting); investigation (supporting); methodology (supporting); software (supporting); supervision (supporting); validation (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Anna Pudło:** Conceptualization (supporting); data curation (supporting); formal analysis (supporting); investigation (supporting); methodology (supporting); supervision (supporting); validation (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Aneta Wojdyło:** Conceptualization (supporting); data curation (supporting); formal analysis (supporting); funding acquisition (supporting); investigation (supporting); methodology (supporting); validation (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Safira Noor Andayani:** Conceptualization (supporting); software (supporting); visualization (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Leonie Margaretha Widya Pangestika:** Conceptualization (supporting); software (supporting); visualization (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Małgorzata Korzeniowska:** Conceptualization (equal); data curation (equal); formal analysis (supporting); funding acquisition (equal); investigation (lead); methodology (equal); project administration (equal); resources (lead); software (supporting); supervision (lead); validation (lead); visualization (supporting); writing – original draft (supporting); writing – review and editing (supporting). **Baoru Yang:** Conceptualization (supporting); funding acquisition (equal); project administration (lead); supervision (equal); writing – original draft (supporting); writing – review and editing (supporting).

Conflict of interest

None.

Ethical approval

Ethics approval was not required for this research.

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