Food Bioscience 53 (2023) 102523

Contents lists available at ScienceDirect

Food Bioscience

journal homepage: www.elsevier.com/locate/fbio

Conventional water bath heating on undried brewer's spent grain: Functionality, fatty acids, volatiles, polyphenolic and antioxidant properties

Joncer Naibaho [a,*], Anna Pudło [a], Łukasz Bobak [a], Aneta Wojdyło [b], Álvaro Alemany López [c], Leonie Margaretha Widya Pangestika [d], Safira Noor Andayani [e], Małgorzata Korzeniowska [a,**], Baoru Yang [f]

[a] Department of Functional Food Products Development, Faculty of Biotechnology and Food Science, Wroclaw University of Environmental and Life Sciences, 51-630, Wroclaw, Poland
[b] Department of Fruit, Vegetable and Plant Nutraceutical Technology, Faculty of Biotechnology and Food Science, Wrocław University of Environmental and Life Sciences, 51-630, Wroclaw, Poland
[c] Faculty of Experimental Sciences, Universidad Miguel Hernández, Alicante, Spain
[d] Faculty of Technobiology, Universitas Atma Jaya Yogyakarta, Yogyakarta, Indonesia
[e] Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Pendidikan Ganesha, 81116, Singaraja, Indonesia
[f] Food Chemistry and Food Development, Department of Life Technologies, University of Turku, 20014, Turku, Finland

ARTICLE INFO

Keywords:
By-product valorization
Sustainability
Thermal exposures
Value-added production

ABSTRACT

Brewers' spent grain (BSG) contains bioactive compounds. It was hypothesized that heating treatments using conventional water bath heating (CWH) on brewers' spent grain (BSG) would modify the functionality, chemical constituents and antioxidant activities of BSG. Different temperatures and time exposures (80, 90 and 100 °C at 15, 30 and 60 min) were applied on fresh undried BSG. CWH at 80 °C increased the amount of flavan-3-ols, while 100 °C at 30 and 60 min improved the ABTS (2,2′-Azinobis-(3-ethylbenzthiazoline-6-sulfonic acid) value. CWH significantly declined saturated fatty acid and enhanced the poly-unsaturated fatty acid. Moreover, CWH discharged pungent, floral, spice and mushroom odor perceptions and formed fruity, sweet and pleasant odor perceptions, as well as essential-oil-related compounds. Additionally, CWH improved water-holding and oil-holding capacities. In conclusion, CWH as a low-cost treatment improved the functionality, fatty acid composition and aromatic profile of BSG.

1. Introduction

The valorization of brewer's spent grain (BSG) has been reviewed as a means to produce functional foods and nutraceutical ingredients (Naibaho & Korzeniowska, 2021). BSG has high nutritional value, including dietary fiber, proteins, fatty acids and phenolic acids, thus potentially possessing benefits for human health (Naibaho & Korzeniowska, 2021). Several treatments, including chemical, physical, enzymatic and combination treatments, have been applied in order to improve yield extracts, biological properties and/or the functional behavior of BSG (Naibaho & Korzeniowska, 2021). Physical treatments including steam explosions, autoclaves, particle size reduction and pulse electric fields have been applied for the treatment of BSG, improving phenolic compound contents and biological properties, intensifying the amount of soluble dietary fiber, enhancing protein functionality and modifying the structure of arabinoxylans (Connolly et al., 2019; Kumari et al., 2019; Martín-García et al., 2020; Verni et al., 2020).

Heating using a water bath is seemingly promising, as it is a low-cost processing alternative that uses simple equipment and is relatively easy to operate. Water baths have been conventionally utilized in food processing and have been compared to advanced thermal-related treatments such as microwave, ultrasound and ohmic heating techniques (Jung et al., 2020; Ye et al., 2022; Zhang et al., 2015). Obviously, newly advanced technology tends to have better performance in modifying the

* Corresponding author.
** Corresponding author.
E-mail addresses: joncer.naibaho@upwr.edu.pl (J. Naibaho), malgorzata.korzeniowska@upwr.edu.pl (M. Korzeniowska).

https://doi.org/10.1016/j.fbio.2023.102523
Received 11 September 2022; Received in revised form 17 February 2023; Accepted 1 March 2023
Available online 2 March 2023

qualities of food products; however, water baths are simple, low-cost and easily reproducible, in terms of their application. The use of a water bath improved the performance of microwave–ultrasound heating with respect to increasing the strength and water-holding capacity of gels (Ye et al., 2022). A water bath also influenced the performance of ultrasound-assisted treatments in improving the properties of the Maillard reaction with respect to chitosan–fructose (Zhang et al., 2015). However, to the best of our knowledge, the conventional water bath heating (CWH) treatment of BSG has not yet been reported.

Therefore, the potential of using a water bath for the thermal treatment of BSG was taken into consideration. This study aimed to evaluate the change in BSG properties due to water bath thermal heating treatments. It was hypothesized that thermal treatments using a water bath would modify functionalities such as water-holding capacity (WHC) and oil-holding capacity (OHC), antioxidant capabilities and chemical constituents, such as phenolic compounds, fatty acid composition and the volatile profile of BSG.

2. Materials and methods

2.1. Materials

2.1.1. BSG and BSG preparation

BSG wet slurry was collected from a local light-beer producer in Wroclaw, Poland. The BSG was then ground to pass 0.2 mm, kept in a polyethylene bag and stored at freezing temperatures (−20 °C) prior to the experiment.

2.1.2. Chemicals and reagents

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

2.2. Experimental design

Ground wet BSG was mixed properly with distilled water at a ratio of 1:1 in a glass beaker. The mixture was then properly closed with aluminum foil. The mixture was heated in a conventional water bath (Julabo TW-12 ECO, Julabo GmbH, Germany) at different temperatures. CWH is typically applied at 85 °C for 30 min. Thus, our experiment was designed just below and above the level of technical CWH; specifically, thermal exposure was conducted at 80, 90, or 100 °C (±1 °C) for time exposures of 15, 30 or 60 min. The treated BSG was dried using an oven dryer at 75 °C overnight (±16 h) to obtain moisture contents below 6% (see Table 1). The samples were ground using a laboratory-scale blender for 5 min with a 10 s pause every 1 min. Samples were packed into aluminum foil and kept at 10 °C for further analysis.

2.3. Analysis of moisture and extracted fat content

Moisture content was measured using the oven method and fat content was measured by using the Soxhlet method (Buchi B-811, Postfach, Liechtenstein), following AOAC 2000 procedures and triplicate applications.

2.4. Analysis of WHC and OHC

The physical properties of BSG were evaluated for WHC and OHC, as described previously (Ktenioudaki et al., 2013). The analysis was conducted in triplicate.

2.5. Methanol extraction, antioxidant analysis and polyphenolic quantification

Methanol extracts were prepared following the procedure described in (Naibaho et al., 2022). *In vitro* antioxidant capabilities for ABTS (2, 2′-Azinobis-(3-ethylbenzthiazoline-6-sulfonic acid) and FRAP (ferric-reducing antioxidant power) were assessed (Naibaho et al., 2022). The extraction was performed in duplicate, and the analysis of antioxidants was performed in triplicate. The quantification of flavan-3-ols and phenolic acids was conducted by UPLC-PDA-FL (Waters Corp, Milford, MA. US) following the procedures described in (Tkacz et al., 2021) and performed in duplicate.

Table 1
Physico-chemical and biological properties of waterbath heating treated spent grain.

Treatments	MC (%)	Fat (%)	WHC (g/g)	OHC (g/g)	ABTS (mmol Trolox/Kg)	FRAP (mmol Trolox/Kg)	Total flavan-3-ols (mg/kg)	Total phenolic acids (mg/kg)	Total polyphenolic compounds (mg/kg)
Control	5.39 ± 0.35^{a}	6.62 ± 0.31^{de}	2.90 ± 0.05^{d}	2.05 ± 0.01^{f}	1.1 ± 0.00^{bc}	0.7 ± 0.01^{ab}	122.79 ± 0.71^{b}	44.29 ± 2.12^{a}	167.07 ± 1.41^{c}
80 °C/15 min	5.18 ± 0.05^{a}	5.88 ± 0.07^{f}	3.50 ± 0.05^{bc}	2.14 ± 0.00^{bc}	0.9 ± 0.00^{cd}	0.3 ± 0.00^{bc}	150.90 ± 0.71^{a}	24.34 ± 0.07^{bc}	175.24 ± 0.78^{ab}
80 °C/30 min	4.50 ± 0.09^{b}	6.40 ± 0.11^{ef}	3.74 ± 0.05^{ab}	2.13 ± 0.00^{cd}	0.9 ± 0.00^{cd}	0.2 ± 0.01^{c}	144.88 ± 0.71^{a}	25.26 ± 0.14^{bc}	170.14 ± 0.85^{bc}
80 °C/60 min	4.25 ± 0.19^{b}	6.91 ± 0.07^{cde}	3.67 ± 0.05^{abc}	2.12 ± 0.00^{d}	0.9 ± 0.00^{cd}	0.4 ± 0.00^{bc}	151.33 ± 0.71^{a}	27.23 ± 0.28^{b}	178.56 ± 0.42^{a}
90 °C/15 min	4.37 ± 0.00^{b}	6.65 ± 0.06^{de}	3.55 ± 0.02^{abc}	2.10 ± 0.00^{e}	0.7 ± 0.00^{d}	0.3 ± 0.00^{bc}	151.33 ± 0.28^{a}	27.09 ± 0.07^{b}	178.41 ± 0.35^{a}
90 °C/30 min	4.48 ± 0.11^{b}	7.35 ± 0.08^{bc}	3.69 ± 0.11^{ab}	2.16 ± 0.00^{a}	0.8 ± 0.01^{d}	0.5 ± 0.02^{abc}	112.64 ± 3.54^{c}	16.81 ± 0.71^{d}	129.45 ± 4.24^{e}
90 °C/60 min	4.34 ± 0.02^{b}	7.07 ± 0.07^{bcd}	3.77 ± 0.13^{a}	2.15 ± 0.00^{ab}	1.0 ± 0.01^{bc}	0.5 ± 0.00^{abc}	108.06 ± 1.41^{c}	22.67 ± 1.16^{c}	130.73 ± 0.26^{de}
100 °C/15 min	4.29 ± 0.22^{b}	6.95 ± 0.21^{cde}	3.59 ± 0.00^{abc}	2.13 ± 0.00^{cd}	0.9 ± 0.01^{cd}	0.3 ± 0.02^{bc}	107.99 ± 1.41^{c}	10.21 ± 0.71^{e}	118.20 ± 2.12^{f}
100 °C/30 min	4.44 ± 0.15^{b}	7.56 ± 0.08^{b}	3.60 ± 0.05^{abc}	2.09 ± 0.00^{e}	1.3 ± 0.00^{a}	0.6 ± 0.00^{ab}	124.38 ± 2.83^{b}	8.97 ± 0.22^{e}	133.35 ± 2.61^{de}
100 °C/60 min	4.25 ± 0.03^{b}	8.13 ± 0.13^{a}	3.41 ± 0.06^{c}	2.09 ± 0.00^{e}	1.3 ± 0.00^{a}	0.8 ± 0.00^{a}	125.48 ± 3.54^{b}	11.97 ± 1.41^{e}	137.45 ± 2.12^{d}

Note: the data is shown as mean ± standard deviation with at least duplicate analysis. Letters show the significant differences from other treatment in the same column ($p < 0.05$). MC: moisture content, WHC: water holding capacity, OHC: oil holding capacity, ABTS: 2,2′-Azinobis-(3-ethylbenzthiazoline-6-sulfonic acid, FRAP: ferric-reducing antioxidant power.

2.6. Analysis of fatty acids composition by GC-MS

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

2.7. Analysis of volatile compounds by GC-MS

The impact of CWH on the volatile compounds of BSG was determined based on a linear function of temperature and time exposure which describes the level of exposures. The study was designed at 3 different levels of temperature and 3 different levels of time exposure. The analysis of volatile compounds was carried out to evaluate the impact of CWH at the lowest, medium, and highest exposure levels. Therefore, the profile of volatile compounds was only conducted at a combination of temperature at 80 ℃, 90 ℃, and 100 ℃ with time exposure at 15 min, 30 min, and 60 min, respectively. In addition, this hypothesis was based on the preliminary results of crude fat content as presented in Table 1. It is well known that volatile compounds are significantly related to fat composition. As presented in Table 1, the increase in temperature and time exposure enhanced the amount of fat content. Treatment at 80 ℃/15 min (lowest exposure level) represented the lowest fat content, while 90 ℃/30 min (medium exposure level) and 100 ℃/60 min (highest exposure level) represented medium and highest fat content, respectively.

The analysis of volatile compounds was carried out following previously described procedures (Dong et al., 2013; Ktenioudaki et al., 2013). Briefly, dried samples were mixed with distilled water at a ratio of 1:2 and closed properly. The volatiles were isolated by headspace solid phase microextraction (HS-SPME) using a GC-MS 5975 C (Agilent J&W, USA). The mixture was heated at 60 °C, and fiber (50/30 μm DVB/CAR/PDMS, Supelco – Sigma-Aldrich, Germany) was exposed to the headspace for 30 min. The length of the fibers in the headspace was kept constant. Helium was used as the carrier gas (1 mL/min). The separation of compounds was performed in a DB-5 column (30 m × 0.25 mm, df = 0.25 l m; Agilent J&W, USA). The injector, ion source and interface temperatures were set at 250, 200 and 260 °C, respectively. The mass spectrometer was operated in an electron impact mode, with the electron energy set at 70 eV and with a scan range of 40–400 m/z. The oven's temperature elevated from 40 to 250 °C at a rate of 4 °C/min, and the temperature was held constant for 5 min. The peak area was measured either by full scanning or by choosing specific fragments. Volatile compounds were tentatively identified using the spectra of reference compounds from NIST.

2.8. Statistical analysis

The data were collected from duplicate treatments and duplicate analyses at the minimum. One-way analysis of variance (ANOVA) and Tukey's post hoc test were performed for significant level at 95% ($p < 0.05$) using Statistica software (version 13.5.0.17, StatSoft GmbH, Germany). Furthermore, principal component analysis (PCA) was performed using the same software (Statistica software).

3. Results and discussion

3.1. Extracted fat content

As observed in Table 1, CWH at 80 °C/15 min lowered the extracted fat content statistically ($p < 0.05$), while 30 and 60 min time exposures generated the same amount of fat content ($p > 0.05$) compared to the control. Furthermore, the use of higher temperatures (90 and 100 °C) and 15 min exposure had the same level of fat content, while longer time exposures (30 and 60 min) increased the extracted fat content. The highest fat content was obtained at 100 °C/60 min, followed by a 100 °C/30 min treatment, while the lowest was at 80 °C/15 min. The fat contents in the current study ranged from 5.88% to 8.13%. The BSG in the current study had a lower value of fat content compared to previous observations, which ranged between 8% and 34% (Naibaho et al., 2021). An improvement in fat content due to the thermal exposure of BSG has been previously observed (Naibaho et al., 2021), and it was reported that this phenomenon may occur due to the ability of high temperatures to break the cell walls of the BSG matrix, thus releasing certain compounds (Ibbett et al., 2019). As a consequence, the modification of chemical constituents, such as dietary fiber, fats and fatty acids, proteins and amino acids and polyphenolic compounds, can be expected.

3.2. WHC and OHC

The results revealed that CWH significantly ($p < 0.05$) improved the WHC of treated BSG from 2.9 g/g to 3.4–3.8 g/g and increased OHC from 2.05 g/g to 2.09–2.16 g/g in the control and treated BSG, respectively. Among the treated groups, there was no significant difference ($p > 0.05$) in WHC, except between 90 and 100 °C at 60 min of heating. A higher OHC value was obtained with lower time exposures, except at 90 °C heating. The variability in WHC and OHC in the current study demonstrated that conventional water bath heating is capable of modifying the functionality of BSG, thus influencing the properties of BSG in the food matrix. This might be due to its influence on the release of certain compounds from BSG matrices, including phenolic and fatty acids and proteins. Moreover, this phenomenon led to different levels of hydroxyl group presence, hydrophobicity and lipophilicity in BSG with respect to the treatments. The WHC level change observed in the current study was in agreement with a previous report (Naibaho et al., 2021), in which the WHC value of autoclaved BSG was in the range of 2.9–3.3 g/g; meanwhile, the OHC values observed in the current study were higher than those reported previously, with OHC being in the range of 0.9–1.9 g/g in autoclaved BSG (Naibaho et al., 2021).

3.3. In vitro antioxidant capabilities

The results showed that CWH at 100 °C with time exposures of 30 or 60 min generated a significantly ($p < 0.05$) higher ABTS, heating at 90 °C with time exposures of 15 or 30 min significantly lowered the ABTS, and other treatments showed the same level as observed in the control. Furthermore, the majority of CWH treatments led to a similar FRAP value as in the control, except when heating at 80 °C for 30 min, under which a significant ($p < 0.05$) decrease was observed. These results demonstrate that CWH slightly influenced the ABTS value. The influence of thermal exposure on the ABTS capability of BSG has been previously observed: It has been reported that autoclaved BSG obtained higher ABTS and FRAP values compared to the control (Naibaho et al., 2022). It was reported that untreated BSG presented 0.8–2.1 mmol Trolox/Kg and 1.1–3.0 mmol Trolox/Kg for ABTS and FRAP, respectively (Naibaho et al., 2020). In other words, CWH-treated BSG had lower antioxidant properties in terms of ABTS and FRAP. ABTS indicates

the ability of the extract to reduce molecular oxygen and hydrogen peroxide (Benzie & Strain, 1996), while FRAP describes how the methanol extracts of BSG alleviate lipid oxidation (Rahman et al., 2021). In this regard, CWH had no influence on the lipid oxidation properties of treated BSG, and it slightly improved its ability for oxygen radical scavenging and hydrogen peroxide neutralization, particularly at 100 °C. This phenomenon may be due to the difference in material preparation, particularly in the drying process. Thermal exposure during drying induced the formation of melanoidin, which is responsible for higher antioxidant properties in BSG (Patrignani & González-Forte, 2021). In a previous report (Naibaho et al., 2020), the BSG was dried using convective drying, which required higher temperatures; in contrast, drying at lower temperatures was conducted in order to reduce the browning effect in materials.

3.4. Quantification of polyphenolic compounds

CWH at 80 °C for all time exposures significantly improved flavan-3-ol contents ($p < 0.05$), while 90 °C CWH decreased flavan-3-ols significantly, except at 60 min, which led to a higher amount than in the control. Treatments with 100 °C CWH produced the same levels of flavan-3-ols as in the control, except at 15 min, under which a lower amount was observed. Furthermore, all CWH decreased the phenolic acid contents. The impact of CWH on the total amount of polyphenolic compounds was seemingly similar as that for flavan-3-ols. The thermal exposure of BSG has been reported for its ability to disrupt cell vacuoles and/or cleave covalent bonds (Rahman et al., 2021). This phenomenon might lead to the modification of lignin solubility (Ohra-aho et al., 2016). Lignin consists of guaiacyl and syringyl functional groups, which bind similarly in all lignins (Ohra-aho et al., 2016). However, the amount and strength of the functional groups may vary (Ohra-aho et al., 2016); in this way, the variability of flavan-3-ols and the decline in phenolic acids due to CWH may have occurred as an effect of different levels of temperature and time exposures. CWH at 80 °C seemed to allow for the release of flavan-3-ols from the matrices, thus increasing their levels, while 90 and 100 °C facilitated the depolymerization and conversion of certain compounds into elementary units, thus decreasing the content of both flavan-3-ols and phenolic acid. Ferulic acids are bound to insoluble structural cellulose or hemicellulose by ester linkages (Sibhatu et al., 2021). Certain treatments might remove the ester-linked ferulic acid from insoluble cellulose, insoluble hemicellulose and lignin matrix, thus causing the content of ferulic acid to fluctuate (Sibhatu et al., 2021). The same phenomenon has been reported previously, in which caffeic acid was depolymerized into ferulic acid (Wojdyło et al., 2014) and ferulic acid was converted into 4-vinylguaiacol (Zago et al., 2022).

Hydroxycinnamic acids were the most abundant phenolic acids in 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). However, their amount and/or presence depends on the extraction method and/or pre-treatment used (Rahman et al., 2021), thus leading to variable amounts of polyphenolic compounds, as was observed in the current study. For instance, it has been identified that caffeic acid was absent in lower temperature treatments, but it was present after exposure to higher temperatures (>100 °C), while sinapinic acid was identified after oven heating at 160 °C (Rahman et al., 2021). However, an investigation of specific phenolic compounds was not included in the current study. Therefore, further investigations should be conducted in order to investigate the impact of CWH on specific phenolic compounds.

3.5. Fatty acid profile

The fatty acid composition of BSG is presented in Table 2. In general, CWH significantly ($p < 0.05$) decreased the saturated fatty acid (SFA) content and increased the poly-unsaturated fatty acid (PUFA) content. The majority of treatments also enhanced the mono-unsaturated fatty acid (MUFA) content, except for the 100 °C treatment for 15 and 30 min, after which a lower amount was obtained compared to the untreated BSG. CWH discharged C17:0 at all levels of temperature and time exposures, while several fatty acids were formed depending on the specific treatment. All CWH treatments induced the formation of C18:0 and

Table 2
Fatty acids composition (% of total fatty acids) of water-bath heating treated spent grain.

Fatty acids (%)	Treatment									
	Control	80 °C/15 min	80 °C/30 min	80 °C/60 min	90 °C/15 min	90 °C/30 min	90 °C/60 min	100 °C/15 min	100 °C/30 min	100 °C/60 min
C13:0	–	0.39 ± 0.01	0.30 ± 0.01	0.29 ± 0.01	–	–	–	–	–	–
C14:0	–	0.36 ± 0.04	0.31 ± 0.01	–	–	–	–	–	–	–
C16:0	40.22 ± 0.00	19.57 ± 0.10	21.96 ± 0.01	22.29 ± 0.02	22.29 ± 0.01	21.30 ± 0.00	21.30 ± 0.01	22.22 ± 0.02	23.66 ± 0.01	21.51 ± 0.01
C16:1	–	0.49 ± 0.01	–	–	–	–	–	–	–	–
C17:0	4.93 ± 0.00	–	–	–	–	–	–	–	–	–
C18:0	–	3.18 ± 0.02	2.98 ± 0.01	3.04 ± 0.01	3.05 ± 0.01	3.13 ± 0.00	3.13 ± 0.01	3.88 ± 0.01	3.88 ± 0.01	3.43 ± 0.01
18:1 (n-9)	19.39 ± 0.00	16.17 ± 0.02	17.76 ± 0.01	17.73 ± 0.02	17.81 ± 0.01	17.90 ± 0.00	17.90 ± 0.01	17.28 ± 0.01	16.29 ± 0.01	17.46 ± 0.01
18:2 (n-6)	32.81 ± 0.00	48.83 ± 0.06	47.38 ± 0.01	47.42 ± 0.02	48.36 ± 0.01	48.11 ± 0.00	48.11 ± 0.01	48.27 ± 0.04	49.51 ± 0.01	48.94 ± 0.01
18:3 (n-3)	2.66 ± 0.00	5.20 ± 0.02	6.05 ± 0.01	5.94 ± 0.01	5.78 ± 0.01	5.95 ± 0.00	5.95 ± 0.00	5.49 ± 0.01	4.96 ± 0.01	5.77 ± 0.01
C20	–	0.79 ± 0.01	0.72 ± 0.02	0.77 ± 0.01	0.78 ± 0.01	0.82 ± 0.00	0.82 ± 0.00	0.82 ± 0.01	–	0.84 ± 0.01
C20:1	–	1.83 ± 0.01	1.81 ± 0.02	1.81 ± 0.01	1.93 ± 0.01	1.98 ± 0.00	1.98 ± 0.01	2.03 ± 0.01	1.71 ± 0.01	2.05 ± 0.01
C20:2	–	0.29 ± 0.01	–	–	–	–	–	–	–	–
C22:0	–	0.79 ± 0.01	0.71 ± 0.02	0.70 ± 0.01	–	0.80 ± 0.00	0.80 ± 0.01	–	–	–
C22:1	–	0.70 ± 0.01	–	–	–	–	–	–	–	–
C24:0	–	0.92 ± 0.01	–	–	–	–	–	–	–	–
C24:1	–	0.51 ± 0.01	–	–	–	–	–	–	–	–
Total SFA	45.15 ± 0.00^{a}	25.99 ± 0.07^{f}	26.98 ± 0.01^{d}	27.10 ± 0.01^{c}	26.12 ± 0.01^{e}	26.06 ± 0.00^{ef}	26.06 ± 0.01^{ef}	26.93 ± 0.02^{d}	27.53 ± 0.01^{b}	25.78 ± 0.01^{g}
Total MUFA	19.39 ± 0.00^{g}	19.69 ± 0.02^{c}	19.58 ± 0.01^{d}	19.54 ± 0.03^{e}	19.74 ± 0.01^{b}	19.89 ± 0.00^{a}	19.89 ± 0.01^{a}	19.31 ± 0.01^{h}	18.00 ± 0.01^{i}	19.51 ± 0.01^{f}
Total PUFA	35.46 ± 0.00^{i}	54.32 ± 0.07^{c}	53.44 ± 0.01^{g}	53.36 ± 0.02^{h}	54.14 ± 0.01^{d}	54.06 ± 0.00^{e}	54.06 ± 0.01^{e}	53.76 ± 0.05^{f}	54.47 ± 0.01^{b}	54.71 ± 0.01^{a}

Note: the data is shown as mean ± standard deviation with at least duplicate analysis. Letters show the significant differences from other treatment in the same row ($p < 0.05$). SFA: saturated fatty acid, MUFA: mono-unsaturated fatty acid, PUFA: poly-unsaturated fatty acid.

C20:1; almost all treatments formed C20:0, except for the 100 °C/30 min treatment; C22:0 was identified after 80 °C treatment for all time exposures, as well as 90 °C at 30 and 60 min; C13:0 was present after all 80 °C treatments, while 14:0 was only identified at 15 and 30 min. However, C16:1, C20:2, C22:1, C24:0 and C24:1 were only identified in BSG treated at 80 °C/15 min.

The results revealed that the main fatty acids in BSG were PUFAs C18:2(n-6) and C18:3(n-3), MUFA C18:1(n-9) and SFA C16:0. These results are in agreement with those previously reported (Mallen & Najdanovic-Visak, 2018). The increase in fatty acid yield has been observed due to an elevation in temperature (Mallen & Najdanovic-Visak, 2018) as a result of the increasing transesterification rate, which simultaneously improved the solubility and mass transfer of triglycerides (Mallen & Najdanovic-Visak, 2018). Increases in UFAs in BSG have also been identified previously as an effect of solid-state fermentation (Tan et al., 2019), which hydrolyzed lipids into fatty acids. In a similar manner, CWH might have induced the hydrolysis of lipids and/or intensified the transesterification rate, thus allowing for the formation of UFAs. Compared to the previous study, the fatty acids formed due to CWH, such as C13:0, C17:0, C20:2, C22:1 and C24:1, were not observed in BSG (Ibarruri et al., 2019); however, these fatty acids have been identified in dried and lyophilized BSG to a lesser extent (Fărcaş et al., 2015). Furthermore, the thermal exposure of BSG allowed for the release of certain functional groups from polysaccharides (Rahman et al., 2021). In this way, CWH might have induced the release of fatty acids from the functional groups of polysaccharides or from cell vacuoles. The results demonstrate that CWH improved the fatty acid properties of BSG, thus facilitating its application in industries such as pharmaceutics, cosmetics and functional foods. PUFAs are well-known for their benefits to human health, while SFAs have been recognized for their role in the induction of non-communicable diseases. Therefore, the ability of CWH to reduce SFA and enhancing PUFA contents might allow for greater benefits with respect to human health.

3.6. Volatile compounds profile

The volatile compound profile of BSG was assessed based on linear elevation treatments from the lowest to highest temperature and time exposure in order to investigate the impact of linear treatments on volatile compounds. Therefore, the evaluation of volatile compounds was carried out for the 80 °C/15 min, 90 °C/30 min and 100 °C/60 min treatments, and the results were compared with those of the untreated BSG. The results of the linear treatment's analysis regarding the volatile compound profile of BSG are presented in Table 3. The results show that the volatile compounds in BSG were quantitatively dominated by aldehydes, followed by ketones and alkanes, while several other groups were also present, including volatile fatty acids, alcohols, furans and others. In general, with higher temperatures and time exposures, the total aldehyde and furan contents will be higher. At the same time, the contents of ketones, alcohols, alkene and other groups declined.

Compared to the control, CWH significantly ($p < 0.05$) decreased the total amount of aldehydes. CWH eliminated 3-methyl-butanal, pentanal, (Z)-2-heptenal and (E)-2-hexenal in BSG. Those compounds have been identified in BSG in previous studies: 3-methyl-butanal has been reported to be responsible for buttery, oily, dark chocolate, cacao and almond odor perception; pentanal is responsible for almond, malt and pungent odor perception; (Z)-2-heptenal is responsible for green and pungent odor perception (Dong et al., 2013; Fărcaş et al., 2015; Ktenioudaki et al., 2013). However, the existence of (E)-2-hexenal has never been reported in BSG. (E)-2-hexenal has been identified as a green leaf volatile, and it has anti-fungal properties and is responsible for unpleasant odor, which deters fungi and insects (Kunishima et al., 2016). 3-Methyl-butanal, pentanal and (Z)-2-heptenal form during fermentation in the brewing process (Dong et al., 2013; Ktenioudaki et al., 2013), while (E)-2-hexenal might appear due to post-harvest handling or was naturally present in barley leaves, as many floral volatiles are present as

Table 3
Volatile compounds of water-bath heating treated spent grain (percentage of peak area).

Volatile compounds	BSG treatments			
	Control	80 °C/ 15 min	90 °C/ 30 min	100 °C/ 60 min
Aldehydes				
Butanal, 3-methyl-	4.39 ± 0.01	–	–	–
Pentanal	1.17 ± 0.01	–	–	–
Hexanal	16.94 ± 0.08	1.76 ± 0.00	15.18 ± 0.34	15.37 ± 0.09
2-Hexenal, (E)-	0.54 ± 0.00	–	–	–
Heptanal	1.23 ± 0.01	1.01 ± 0.01	1.05 ± 0.04	1.31 ± 0.07
2-Heptenal, (Z)-	1.10 ± 0.01	–	–	–
2,4-Heptadienal, (E,E)-	0.52 ± 0.00	–	–	0.38 ± 0.03
Octanal	–	–	–	1.34 ± 0.04
2-Octenal, (E)-	3.55 ± 0.01	3.15 ± 0.11	4.53 ± 0.12	2.29 ± 0.14
Nonanal	10.90 ± 0.15	10.08 ± 0.02	7.23 ± 0.09	8.98 ± 0.01
2-Nonenal, (E)-	3.00 ± 0.01	2.19 ± 0.08	3.04 ± 0.11	2.84 ± 0.07
2,4-Nonadienal, (E,E)-	0.86 ± 0.01	0.62 ± 0.04	0.53 ± 0.04	0.39 ± 0.03
Decanal	1.88 ± 0.02	1.87 ± 0.08	1.73 ± 0.08	1.50 ± 0.08
2,4-Decadienal, (E,E)-	–	–	1.42 ± 0.08	5.02 ± 0.04
Undecanal	0.35 ± 0.00	–	–	3.59 ± 0.06
Octadecanal, 2-bromo-	–	0.59 ± 0.04	–	1.78 ± 0.01
Benzaldehyde	4.83 ± 0.03	11.80 ± 0.14	4.76 ± 0.08	4.81 ± 0.00
Benzeneacetaldehyde	6.96 ± 0.09	3.34 ± 0.05	7.40 ± 0.09	7.06 ± 0.11
Ketones				
Acetophenone	–	0.31 ± 0.01	–	–
2-Hexanone, 5-methyl-	–	–	0.57 ± 0.03	–
2-Heptanone	1.21 ± 0.05	–	0.70 ± 0.04	1.09 ± 0.04
5-Hepten-2-one, 6-methyl-	0.60 ± 0.05	–	–	–
3-Octen-2-one, (E)-	1.92 ± 0.14	1.39 ± 0.08	3.38 ± 0.04	0.95 ± 0.07
3-Octanone, 2-methyl-	0.86 ± 0.02	–	–	–
3,5-Octadien-2-one, (E,E)-	7.36 ± 0.47	6.80 ± 0.21	10.04 ± 0.38	6.94 ± 0.30
5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	0.43 ± 0.02	0.31 ± 0.00	–	–
2-Undecanone	–	6.48 ± 0.15	–	2.56 ± 0.04
2(3H)-Furanone, 5-heptyldihydro-	0.61 ± 0.02	0.30 ± 0.01	0.42 ± 0.02	–
Alcohols				
Ethanol, 2-(9,12-octadecadienyloxy)-, (Z,Z)-	–	0.33 ± 0.01	–	–
1-Hexanol	–	0.29 ± 0.02	–	–
1-Hexanol, 2-ethyl-	–	4.23 ± 0.02	–	–
1-Octen-3-ol	1.76 ± 0.14	1.16 ± 0.02	2.34 ± 0.04	1.49 ± 0.04

(continued on next page)

Table 3 (*continued*)

Volatile compounds	BSG treatments			
	Control	80 °C/ 15 min	90 °C/ 30 min	100 °C/ 60 min
2-Octen-1-ol, (Z)-	0.42 ± 0.02	0.46 ± 0.01	0.43 ± 0.02	0.45 ± 0.03
5-Octen-2-yn-4-ol	–	–	0.59 ± 0.02	–
Nona-3,5-dien-2-ol	0.55 ± 0.02	–	–	–
9-Oxabicyclo[6.1.0]nonan-4-ol	–	–	0.60 ± 0.04	–
2-Nitrohept-2-en-1-ol	0.39 ± 0.01	–	–	–
4,4,6-Trimethyl-cyclohex-2-en-1-ol	1.08 ± 0.06	–	–	–
2-Butyl-2,7-octadien-1-ol	0.56 ± 0.04	–	–	–
1-Decanol, 2-hexyl-	–	–	–	0.73 ± 0.04
1-Tetradecanol	0.37 ± 0.03	–	–	–
1-Hexadecanol	1.09 ± 0.09	–	0.60 ± 0.03	–
n-Nonadecanol-1	–	–	0.42 ± 0.03	–
4,4,6-Trimethyl-cyclohex-2-en-1-ol	–	–	0.71 ± 0.01	–
9-(3,3-Dimethyloxiran-2-yl)-2,7-dimethylnona-2,6-dien-1-ol	–	–	–	0.25 ± 0.01
Furan				
Furan, 2-pentyl-	7.44 ± 0.46	7.28 ± 0.07	8.47 ± 0.16	9.22 ± 0.19
Alkane				
Tridecane	4.62 ± 0.05	5.36 ± 0.00	6.66 ± 0.05	6.91 ± 0.08
Tetradecane, 2,6,10-trimethyl-	1.94 ± 0.04	–	–	–
Tetradecane	1.09 ± 0.05	5.06 ± 0.00	0.63 ± 0.03	–
1-Pentadecene	–	–	0.44 ± 0.01	0.53 ± 0.01
Heptacosane	–	–	1.42 ± 0.08	–
Hexadecane, 1,1-bis (dodecyloxy)-	–	0.81 ± 0.08	0.37 ± 0.01	–
Nonadecane	0.40 ± 0.01	–	–	–
Dodecane	3.32 ± 0.09	7.55 ± 0.07	7.11 ± 0.11	6.69 ± 0.01
Octadecane, 3-ethyl-5-(2-ethylbutyl)-	–	2.15 ± 0.08	0.72 ± 0.01	1.14 ± 0.02
Undecane	–	–	0.58 ± 0.03	0.54 ± 0.01
Eicosane	–	–	0.51 ± 0.01	–
Heneicosane	–	–	0.97 ± 0.02	–
Fatty acids				
Hexanoic acid	0.93 ± 0.05	1.91 ± 0.04	–	1.96 ± 0.03
Dodecanoic acid, 3-hydroxy-	–	–	0.41 ± 0.02	–
Others				
D-Limonene	1.58 ± 0.09	–	1.97 ± 0.03	1.54 ± 0.05
Benzeneethanamine, 2,5-difluoro-β,3,4-trihydroxy-N-methyl-	1.26 ± 0.07	–	–	0.35 ± 0.02
Benzene, 1-methyl-3-(1-methylethyl)-	–	0.43 ± 0.01	0.62 ± 0.02	–
5-Benzylidene-3-(3,4-dimethylanilinomethyl)-2,4-thiazolidinedione	–	–	0.34 ± 0.01	–
Ethyl Acetate	–	8.36 ± 0.04	–	–
1R-α-Pinene	–	0.35 ± 0.01	–	–
Oxime-, methoxy-phenyl-	–	2.28 ± 0.04	1.09 ± 0.01	–
TOTAL				
Aldehydes	58.21 ± 0.07^{a}	36.40 ± 0.10^{d}	46.87 ± 0.08^{c}	56.67 ± 0.22^{b}
Ketones	12.99 ± 0.63^{b}	15.58 ± 0.13^{a}	15.11 ± 0.46^{a}	11.54 ± 0.29^{b}
Alcohols	6.22 ± 0.11^{a}	6.48 ± 0.03^{a}	5.70 ± 0.18^{b}	2.92 ± 0.05^{c}
Furans	7.44 ± 0.46^{bc}	7.28 ± 0.03^{c}	8.47 ± 0.16^{ab}	9.22 ± 0.19^{a}
Alkane	11.38 ± 0.02^{d}	20.93 ± 0.03^{a}	19.42 ± 0.05^{b}	15.80 ± 0.12^{c}
Fatty acid	0.93 ± 0.05^{b}	1.91 ± 0.04^{a}	0.41 ± 0.02^{c}	1.96 ± 0.03^{a}
Others	2.83 ± 0.16^{c}	11.42 ± 0.07^{a}	4.01 ± 0.07^{b}	1.89 ± 0.07^{d}

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

anti-fungal compounds in plants.

Furthermore, CWH induced the formation of octanal, (E,E)-2,4-decadienal and 2-bromo-octadecanal. Octanal has been identified in barley and malt, but it was absent in BSG (Fărcaş et al., 2015). Therefore, CWH may have reformed the octanal as in its original form. Octanal exhibits fat, soap, lemon and green odor perceptions (Dong et al., 2013). (E,E)-2,4-decadienal has not been identified in BSG; however, it was present in bread prepared with dried distilled grain, and it was responsible for rancid odor perceptions (Roth et al., 2016). However, this odor had an odor activity value at 23.4%, which is much higher than that observed in the current study. The highest amount of (E,E)-2,4-decadienal in the current study was 5.02%. In this way, rancid odor might not be detected by the human sense of smell.

CWH at 80 °C/15 min and 90 °C/30 min significantly increased ($p < 0.05$) the total ketones in BSG, while 100 °C/60 min generated the same level as in the control. CWH discharged 6-methyl-5-hepten-2-one and 2-methyl-3-octanone in all elevation levels. 6-Methyl-5-hepten-2-one is responsible for herb, oily, pungent, pear, pepper and mushroom odor perceptions (Dong et al., 2013), and it has been reported to be present in BSG-added crackers (O'Shea et al., 2017) and grain malts (Dong et al., 2013). The formation of several ketones was identified after CWH treatment, such as acetophenone (80 °C/15 min), 5-methyl-2-hexanone (90 °C/30 min) and 2-undecanone (80 °C/15 min and 100 °C/60 min). Acetophenone represents a sweet, floral and almond odor perception (Fărcaş et al., 2015). Notably, 2-undecanone and 5-methyl-2-hexanone have never been reported in BSG; however, 2-undecanone has been identified as the second most-abundant ketone in UHT milk (Dursun et al., 2017), while 5-methyl-2-hexanone was present in black tea (Yan et al., 2022). Methyl ketones predominantly originate in the lipid fraction (Dursun et al., 2017); thus, their presence may depend on lipid degradation due to thermal exposure.

CWH discharged the majority of alcohols present in untreated BSG: eight alcohols were identified in the original BSG, while only two

remained in the CWH-treated BSG, including 1-octen-3-ol and (Z)-2-octen-1-ol. Several alcohols formed due to CWH, including (Z,Z)-2-(9,12-octadecadienyloxy)-ethanol, 1-hexanol and 2-ethyl-1-hexanol at 80 °C/15 min; 5-octen-2-yn-1-ol, 9-oxabicyclo[6.1.0]nonan-4-ol, n-nonadecanol-1 and 4,4,6-trimethyl-cyclohex2-en-1-ol at 90 °C/30 min; and 2-hexyl-1-decanol and 9-(3,3-Dimethyloxiran-2-yl)-2,7-dimethylnona-2,6-dien-1-ol at 100 °C/60 min. Among those formed alcohol compounds, only 1-hexanol and 2-ethyl-1-hexanol have been identified in grain (Buśko et al., 2010; Dong et al., 2015), which are responsible for a resin, flower and green odor perception (Dong et al., 2013). Meanwhile, (Z,Z)-2-(9,12-octadecadienyloxy)-ethanol, 5-octen-2-yn-4-ol, 9-oxabicyclo[6.1.0]nonan-4-ol, N-nonadecanol-1 and 2-hexyl-1-decanol have been observed as phytochemical constituents in several plant extracts (Abirami & Gomathi, 2022; Nazir et al., 2021).

The CWH treatment generated higher levels of alkanes. 2,6,10-Trimethyl-tetradecane and nonadecane were absent due to the treatment; however, several compounds formed, including heptacosane, 1,1-bis (dodecyloxy)-hexadecane, 3-ethyl-5- (2-ethylbutyl)- octadecane, undecane, eicosane and heneicosane. These compounds have not been previously identified in BSG. However, undecane and eicosane have been reported to be present in grain (Buśko et al., 2010), while heneicosane has been observed in sorghum grain tea (Xiong et al., 2020). Other compounds, including 2,6,10-trimethyl-tetradecane, nonadecane, heptacosane, 1,1-bis(dodecyloxy)-hexadecane and 3-ethyl-5-(2-ethylbutyl)-octadecane have been identified in essential oils and as micro-organism secondary metabolites (Alqahtani et al., 2022; Wei & Fan, 2020).

Additionally, the 90 °C/30 min CWH treatment induced the formation of 3-hydroxy-dodecanoic acid and 2,4-thiazolidinedione; 80 °C/15 min CWH led to the formation of ethyl acetate and 1R-α-Pinene; 1-methyl-3-(1-methylethyl)-benzene and methoxy-phenyl-oxime were identified in both 80 °C/15 min and 90 °C/30 min treatments; 1-pentadecene (an essential oil) was identified in 90 °C/30 min and 100 °C/60 min treatments. The ability of CWH to degrade certain compounds while forming others might be beneficial for the further valorization of BSG. It was discovered that most degraded compounds are responsible for pungent, floral and spice odor perception, while the formed compounds are responsible for certain pleasant perceptions, such as fruity, sweet and essential oil odors. Therefore, such conversions are expected to broaden the utilization of BSG in food ingredients.

3.7. Principal component analysis (PCA)

PCA was conducted with respect to the linear elevation treatments, as in the volatile compound analysis in addition to the untreated BSG. As shown in Fig. 1, untreated BSG tended to be aligned with higher total polyphenolics and SFAs. CWH at lower time and thermal exposure (80 °C/15 min) significantly increased the presence of flavan-3-ols, ketones and alcohols, as well as other volatile compounds. Increasing the temperature and time exposure (to 90 °C/30 min) seemed to improve MUFA and PUFA formation, and it enhanced the functional properties of BSG. Furthermore, CWH treatments at 100 °C/60 min increased the fat content, aldehyde content and antioxidant properties of BSG.

In summary, different temperature and time exposure levels can be utilized depending on the target compounds. This study provides beneficial initial information for further investigations, including those focused on other biological properties, amino acids and peptides, aromatic compounds and specific phenolic compounds.

4. Conclusions

As was hypothesized, it was demonstrated the improvements in the functionality of BSG, including WHC and OHC, after CWH treatment. Treatment at 100 °C for 30 or 60 min generated a higher ABTS capability, while the majority of treatments had no significant influence on FRAP levels. All treatments at 80 °C led to higher total flavan-3-ol contents, while all treatments decreased the total phenolic acids. A significant increase in the amount of PUFAs was observed due to CWH treatments converting SFAs into double-bond fatty acids, thus allowing for the higher production of PUFAs from BSG and potentially promoting its use as a functional food ingredient or for nutraceutical purposes. Moreover, CWH tended to degrade the pungent, floral, spice and mushroom odor perceptions of untreated BSG while inducing the formation of compounds responsible for fruity, sweet and pleasant odors, as well as essential oil-related compounds. The further investigation of other *in vitro* antioxidant activities is seemingly important, particularly in relation to the PUFA's composition, as well as the identification of key aromatic compounds via sensory and olfactory analyses.

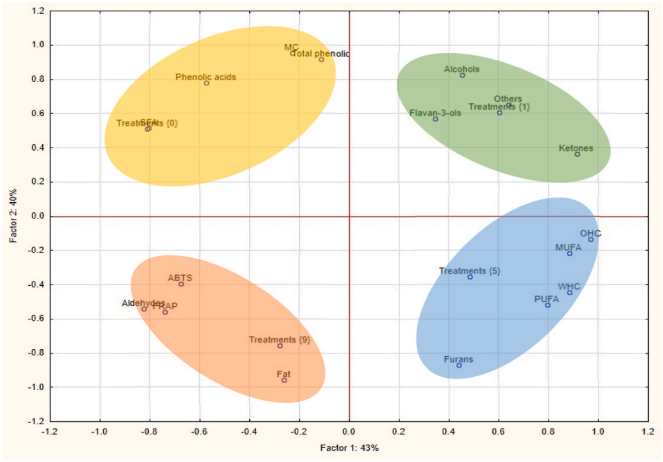

Fig. 1. Principal component analysis (PCA) of conventional water-bath heating on chemical composition, antioxidant properties and techno-functionality of treated spent grain (MC: moisture content, SFA: saturated fatty acid, ABTS: 2,2′-Azinobis-(3-ethylbenzthiazoline-6-sulfonic acid), FRAP: ferric-reducing antioxidant power, MUFA: mono-unsaturated fatty acid, PUFA: poly-unsaturated fatty acid, WHC: water holding capacity, OHC: Oil holding capacity).

Author contributions

Joncer Naibaho: conceptualization, methodology, validation, formal analysis, investigation, writing-original draft preparation, writing-review and editing, funding acquisition.

Anna Pudło: methodology, validation, formal analysis, investigation, writing-review and editing.

Łukasz Bobak: methodology, validation, formal analysis, investigation, writing-review and editing.

Aneta Wojdyło: methodology, validation, formal analysis, investigation, writing-review and editing.

Álvaro Alemany López: methodology, formal analysis, writing-review and editing.

Leonie Margaretha Widya Pangestika: writing-original draft preparation, writing-review and editing.

Safira Noor Andayani: writing-original draft preparation, writing-review and editing.

Małgorzata Korzeniowska: conceptualization, methodology, validation, investigation, resources, writing-review and editing, supervision, project administration, and funding acquisition.

Baoru Yang: writing-review and editing, project administration, and funding acquisition.

Declaration of competing interest

None.

Data availability

The data has been included in the manuscript

Acknowledgements

This work was supported by UPWR 2.0, international and interdisciplinary programme of development of Wrocław University of Environmental and Life Sciences, co-financed by the European Social Fund under the Operational Programme Knowledge Education Development 2014–2020: Axis III Higher education for the economy and development; Action 3.5. Comprehensive programmes for schools of higher education (POWR.03.05.00–00-Z062/18).

It was also supported by ERA-NET CO-FUND Horizon 2020 - FACCE SURPLUS Sustainable and Resilient Agriculture for Food and Non-Food Systems and PROWASTE Protein-fibre biorefinery for scattered material streams (2019–2021).

References

Abirami, D., & Gomathi, R. (2022). Target and candidate agents for diabetes treatment in the framework of the food nexus. *Energy Nexus, 5*, Article 100041. https://doi.org/10.1016/j.nexus.2022.100041

Alqahtani, S. S., Moni, S. S., Sultan, M. H., Ali Bakkari, M., Madkhali, O. A., Alshahrani, S., Makeen, H. A., Joseph Menachery, S., ur Rehman, Z., Shamsher Alam, M., Mohan, S., Eltaib Elmobark, M., Banji, D., & Z. Sayed-Ahmed, M. (2022). Potential bioactive secondary metabolites of *Actinomycetes sp.* Isolated from rocky soils of the heritage village Rijal Alma, Saudi Arabia. *Arabian Journal of Chemistry, 15*(5), Article 103793. https://doi.org/10.1016/j.arabjc.2022.103793

Benzie, I. F. F., & Strain, J. J. (1996). The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": The FRAP assay. *Analytical Biochemistry, 239*(1), 70–76. https://doi.org/10.1006/abio.1996.0292

Buśko, M., Jeleń, H., Góral, T., Chmielewski, J., Stuper, K., Szwajkowska-Michałek, L., Tyrakowska, B., & Perkowski, J. (2010). Volatile metabolites in various cereal grains. *Food Additives & Contaminants: Part A, 27*(11), 1574–1581. https://doi.org/10.1080/19440049.2010.506600

Connolly, A., Cermeño, M., Crowley, D., O'Callaghan, Y., O'Brien, N. M., & FitzGerald, R. J. (2019). Characterisation of the in vitro bioactive properties of alkaline and enzyme extracted brewers' spent grain protein hydrolysates. *Food Research International, 121*, 524–532. https://doi.org/10.1016/j.foodres.2018.12.008

Dong, L., Hou, Y., Li, F., Piao, Y., Zhang, X., Zhang, X., Li, C., & Zhao, C. (2015). Characterization of volatile aroma compounds in different brewing barley cultivars: Characterization of volatile aroma compounds in brewing barley. *Journal of the Science of Food and Agriculture, 95*(5), 915–921. https://doi.org/10.1002/jsfa.6759

Dong, L., Piao, Y., Zhang, X., Zhao, C., Hou, Y., & Shi, Z. (2013). Analysis of volatile compounds from a malting process using headspace solid-phase micro-extraction and GC–MS. *Food Research International, 51*(2), 783–789. https://doi.org/10.1016/j.foodres.2013.01.052

Dursun, A., Güler, Z., & Şekerli, Y. E. (2017). Characterization of volatile compounds and organic acids in ultra-high-temperature milk packaged in tetra brik cartons. *International Journal of Food Properties, 20*(7), 1511–1521. https://doi.org/10.1080/10942912.2016.1213280

Fărcaş, A. C., Socaci, S. A., Dulf, F. V., Tofană, M., Mudura, E., & Diaconeasa, Z. (2015). Volatile profile, fatty acids composition and total phenolics content of brewers' spent grain by-product with potential use in the development of new functional foods. *Journal of Cereal Science, 64*, 34–42. https://doi.org/10.1016/j.jcs.2015.04.003

Ibarruri, J., Cebrián, M., & Hernández, I. (2019). Solid state fermentation of brewer's spent grain using *Rhizopus sp.* to enhance nutritional value. *Waste and Biomass Valorization, 10*(12), 3687–3700. https://doi.org/10.1007/s12649-019-00654-5

Ibbett, R., White, R., Tucker, G., & Foster, T. (2019). Hydro-mechanical processing of brewer's spent grain as a novel route for separation of protein products with differentiated techno-functional properties. *Innovative Food Science & Emerging Technologies, 56*, Article 102184. https://doi.org/10.1016/j.ifset.2019.102184

Jung, H., Moon, J. H., Park, J. W., & Yoon, W. B. (2020). Texture of surimi-canned corn mixed gels with conventional water bath cooking and ohmic heating. *Food Bioscience, 35*, Article 100580. https://doi.org/10.1016/j.fbio.2020.100580

Ktenioudaki, A., O'Shea, N., & Gallagher, E. (2013). Rheological properties of wheat dough supplemented with functional by-products of food processing: Brewer's spent grain and apple pomace. *Journal of Food Engineering, 116*(2), 362–368. https://doi.org/10.1016/j.jfoodeng.2012.12.005

Kumari, B., Tiwari, B. K., Walsh, D., Griffin, T. P., Islam, N., Lyng, J. G., Brunton, N. P., & Rai, D. K. (2019). Impact of pulsed electric field pre-treatment on nutritional and polyphenolic contents and bioactivities of light and dark brewer's spent grains. *Innovative Food Science & Emerging Technologies, 54*, 200–210. https://doi.org/10.1016/j.ifset.2019.04.012

Kunishima, M., Yamauchi, Y., Mizutani, M., Kuse, M., Takikawa, H., & Sugimoto, Y. (2016). Identification of (Z)-3:(E)-2-hexenal isomerases essential to the production of the leaf aldehyde in plants. *Journal of Biological Chemistry, 291*(27), 14023–14033. https://doi.org/10.1074/jbc.M116.726687

Mallen, E., & Najdanovic-Visak, V. (2018). Brewers' spent grains: Drying kinetics and biodiesel production. *Bioresource Technology Reports, 1*, 16–23. https://doi.org/10.1016/j.biteb.2018.01.005

Martín-García, B., Tylewicz, U., Verardo, V., Pasini, F., Gómez-Caravaca, A. M., Caboni, M. F., & Dalla Rosa, M. (2020). Pulsed electric field (PEF) as pre-treatment to improve the phenolic compounds recovery from brewers' spent grains. *Innovative Food Science & Emerging Technologies, 64*, Article 102402. https://doi.org/10.1016/j.ifset.2020.102402

McCarthy, A. L., O'Callaghan, Y. C., Neugart, S., Piggott, C. O., Connolly, A., Jansen, M. A. K., Krumbein, A., Schreiner, M., FitzGerald, R. J., & O'Brien, N. M. (2013). The hydroxycinnamic acid content of barley and brewers' spent grain (BSG) and the potential to incorporate phenolic extracts of BSG as antioxidants into fruit beverages. *Food Chemistry, 141*(3), 2567–2574. https://doi.org/10.1016/j.foodchem.2013.05.048

Naibaho, J., & Korzeniowska, M. (2021). Brewers' spent grain in food systems: Processing and final products quality as a function of fiber modification treatment. *Journal of Food Science, 86*(5), 1532–1551. https://doi.org/10.1111/1750-3841.15714

Naibaho, J., Korzeniowska, M., Wojdyło, A., Figiel, A., Yang, B., Laaksonen, O., Foste, M., Vilu, R., & Viiard, E. (2020). The potential of spent barley as a functional food ingredient: Study on the comparison of dietary fiber and bioactivity. In Proceedings of. *The 1st International Electronic Conference on Food Science and Functional Foods, 86*. https://doi.org/10.3390/foods_2020-08486

Naibaho, J., Korzeniowska, M., Wojdyło, A., Figiel, A., Yang, B., Laaksonen, O., Foste, M., Vilu, R., & Viiard, E. (2021). Fiber modification of brewers' spent grain by autoclave treatment to improve its properties as a functional food ingredient. *LWT - Food Science and Technology, 149*, Article 111877. https://doi.org/10.1016/j.lwt.2021.111877

Naibaho, J., Wojdyło, A., Korzeniowska, M., Laaksonen, O., Föste, M., Kütt, M.-L., & Yang, B. (2022). Antioxidant activities and polyphenolic identification by UPLC-MS/MS of autoclaved brewers' spent grain. *LWT - Food Science and Technology*. , Article 113612. https://doi.org/10.1016/j.lwt.2022.113612

Nazir, S., El-Sherif, A. A., Abdel-Ghani, N. T., Ibrahim, M. A. A., Hegazy, M.-E. F., & Atia, M. A. M. (2021). *Lepidium sativum* secondary metabolites (essential oils): *In vitro* and *in silico* studies on human hepatocellular carcinoma cell lines. *Plants, 10*(9), 1863. https://doi.org/10.3390/plants10091863

Nowacki, D., Martynowicz, H., Skoczyńska, A., Wojakowska, A., Turczyn, B., Bobak, Ł., Trziszka, T., & Szuba, A. (2017). Lecithin derived from ω-3 PUFA fortified eggs decreases blood pressure in spontaneously hypertensive rats. *Scientific Reports, 7*(1), Article 12373. https://doi.org/10.1038/s41598-017-12019-w

Ohra-aho, T., Niemi, P., Aura, A.-M., Orlandi, M., Poutanen, K., Buchert, J., & Tamminen, T. (2016). Structure of brewer's spent grain lignin and its interactions with gut microbiota *in vitro*. *Journal of Agricultural and Food Chemistry, 64*(4), 812–820. https://doi.org/10.1021/acs.jafc.5b05535

O'Shea, N., Kilcawley, K. N., & Gallagher, E. (2017). Aromatic composition and physicochemical characteristics of crackers containing barley fractions. *Cereal Chemistry Journal, 94*(3), 611–618. https://doi.org/10.1094/CCHEM-10-16-0256-R

Patrignani, M., González-Forte, L., & del, S. (2021). Characterisation of melanoidins derived from Brewers' spent grain: New insights into their structure and antioxidant activity. *International Journal of Food Science and Technology, 56*(1), 384–391. https://doi.org/10.1111/ijfs.14653

Rahman, M. J., Malunga, L. N., Eskin, M., Eck, P., Thandapilly, S. J., & Thiyam-Hollander, U. (2021). Valorization of heat-treated brewers' spent grain through the identification of bioactive phenolics by UPLC-PDA and evaluation of their antioxidant activities. *Frontiers in Nutrition, 8*, Article 634519. https://doi.org/10.3389/fnut.2021.634519

Roth, M., Schuster, H., Kollmannsberger, H., Jekle, M., & Becker, T. (2016). Changes in aroma composition and sensory properties provided by distiller's grains addition to bakery products. *Journal of Cereal Science, 72*, 75–83. https://doi.org/10.1016/j.jcs.2016.10.002

Sibhatu, H. K., Anuradha Jabasingh, S., Yimam, A., & Ahmed, S. (2021). Ferulic acid production from brewery spent grains, an agro-industrial waste. *LWT - Food Science and Technology, 135*, Article 110009. https://doi.org/10.1016/j.lwt.2020.110009

Tan, Y. X., Mok, W. K., Lee, J., Kim, J., & Chen, W. N. (2019). Solid state fermentation of brewers' spent grains for improved nutritional profile using *Bacillus subtilis WX-17*. *Fermentation, 5*(3), 52. https://doi.org/10.3390/fermentation5030052

Tkacz, K., Wojdyło, A., Turkiewicz, I. P., & Nowicka, P. (2021). Triterpenoids, phenolic compounds, macro- and microelements in anatomical parts of sea buckthorn (*Hippophaë rhamnoides L.*) berries, branches and leaves. *Journal of Food Composition and Analysis, 103*, Article 104107. https://doi.org/10.1016/j.jfca.2021.104107

Verni, M., Pontonio, E., Krona, A., Jacob, S., Pinto, D., Rinaldi, F., Verardo, V., Díaz-de-Cerio, E., Coda, R., & Rizzello, C. G. (2020). Bioprocessing of brewers' spent grain enhances its antioxidant activity: Characterization of phenolic compounds and bioactive peptides. *Frontiers in Microbiology, 11*, 1831. https://doi.org/10.3389/fmicb.2020.01831

Wei, Q., & Fan, W. (2020). Compositions of volatile oil from flowers, leaves and stems of *Triadica sebifera*. *Journal of Essential Oil Bearing Plants, 23*(3), 633–637. https://doi.org/10.1080/0972060X.2020.1811779

Wojdyło, A., Figiel, A., Lech, K., Nowicka, P., & Oszmiański, J. (2014). Effect of convective and vacuum–microwave drying on the bioactive compounds, color, and antioxidant capacity of sour cherries. *Food and Bioprocess Technology, 7*(3), 829–841. https://doi.org/10.1007/s11947-013-1130-8

Xiong, Y., Zhang, P., Johnson, S., Luo, J., & Fang, Z. (2020). Comparison of the phenolic contents, antioxidant activity and volatile compounds of different sorghum varieties during tea processing. *Journal of the Science of Food and Agriculture, 100*(3), 978–985. https://doi.org/10.1002/jsfa.10090

Yan, T., Lin, J., Zhu, J., Ye, N., Huang, J., Wang, P., Jin, S., Zheng, D., & Yang, J. (2022). Aroma analysis of Fuyun 6 and Jinguanyin black tea in the Fu'an area based on E-nose and GC–MS. *European Food Research and Technology, 248*, 947–961. https://doi.org/10.1007/s00217-021-03930-8

Ye, Y., Liu, X., Bai, W., Zhao, W., Zhang, Y., Dong, H., & Pan, Z. (2022). Effect of microwave-ultrasonic combination treatment on heating-induced gel properties of low-sodium tilapia surimi during gel setting stage and comparative analysis. *LWT - Food Science and Technology, 161*, Article 113386. https://doi.org/10.1016/j.lwt.2022.113386

Zago, E., Tillier, C., De Leener, G., Nandasiri, R., Delporte, C., Bernaerts, K. V., & Shavandi, A. (2022). Sustainable production of low molecular weight phenolic compounds from Belgian brewers' spent grain. *Bioresource Technology Reports, 17*, Article 100964. https://doi.org/10.1016/j.biteb.2022.100964

Zhang, H., Yang, J., & Zhao, Y. (2015). High intensity ultrasound assisted heating to improve solubility, antioxidant and antibacterial properties of chitosan-fructose Maillard reaction products. *LWT - Food Science and Technology, 60*(1), 253–262. https://doi.org/10.1016/j.lwt.2014.07.050